THE COMPOSITION OF MIXED VAPORS, I

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It has long been known that only in the cases of a chemical compound absolutely pure, and of a few two-component systems which show a maximum or minimum vapor-pressure is the percentage composition of the vapor phase the same as that of the liquid phase with which it is in equilibrium. From the slight knowledge of this subject has been deduced the theory of fractional distillation to cover the cases where both components are volatile, that is when their boiling-points do not lie too far apart. When, however, as in the case of a salt and water, there is a great range of temperature between the boiling-points, the assumption is made that the component with the higher boiling-point is non-volatile, and on this rests the present day theory of the rise of the boiling-point in dilute solutions. Of course there can be no absolute division of chemical bodies into volatile and non-volatile classes; everything depends on the conditions of the experiment. Any theory, therefore, which is based on the relative non-volatility of one of the components cannot be of general service. It is unfortunate that the majority of physical chemists appears to be satisfied with the theory which applies not to the general, but to the particular case, and even then for very dilute solutions only—and leave out of the range of their research the examination of dilute solutions where both components are volatile.

This may therefore be given as one reason why it is that the experimental side of the determination of vapor compositions has been so poorly developed; but this cannot explain why the organic chemist has failed to use the best methods in examining the possibilities of separation of the components in mixtures. The truth of this statement is supported by the paucity of the

cases given in chemical literature where there has been deter-
mined with *any* degree of accuracy the compositions of liquid
and vapor phases which are in equilibrium at any pressure
whatever, while the cases exemplifying separations carried out
under the ordinary conditions of laboratory or actual technical
work have (so far as the writer is aware) not been attacked at
all. The scope of the field is hence very great.

Another reason, and one perhaps more important, is that
such determinations have hitherto been made only with great
trouble. All methods which have been employed have required
that the vapor shall be removed from above the solution, con-
densed, and then analyzed by titration,[1] surface tension,[1] optical[2]
or density[3] methods or by ultimate chemical analysis.[4] The ob-
jection which must be raised to every method of vapor composi-
tion determination is that, since the composition of the vapor is
different from that of the solution, its continuous removal for the
purpose of analysis changes the composition of the solution with
which it was in equilibrium. An instance of the extent of this
change will be shown later in the discussion of the results
obtained by Brown.[3]

The method whose description and illustration is the
especial object of this paper rests to a certain extent under the
same disadvantage as all previous ones, but it is believed that
easily determined corrections may be introduced which will ren-
der it exact in its determination of vapor composition ; and
although laboratory experience is disclosing some imperfections
in the apparatus used, it has been thought advisable to publish
the method and the few results obtained by its use up to the
present.

Expressed very briefly the new method suggested is this :
The condensed vapor is returned to a small receiver within the
larger flask containing the solution whose boiling-point is being
taken (pressure constant), and in this receiver the condensed

[1] Duclaux. Ann. Chim. Phys. (5) **14,** 305 (1878).
[2] Lehfeldt. Phil. Mag. [5] **40,** 398 (1895) ; **46,** 42 (1898).
[3] Brown. Jour. Chem. Soc. **35,** 547 (1879) ; **39,** 304 (1881).
[4] Linebarger. Jour. Am. Chem. Soc. **17,** 617 (1895).

vapor is made to boil. From this boiling-point one may, by consulting the boiling-point curve of the two liquids, determine with a very fair degree of accuracy the composition of the condensed vapor.

It is thus apparent that first of all there must be found the boiling-point curve for the two liquids. The compounds which were first used in this work were acetone and water, and as no complete data could be found from which the curve for these substances could be constructed, it was necessary first of all to determine the curve by experiment.

The boiling-point of pure acetone was taken, making use of the Beckmann apparatus and then weighed amounts of water were added and the corresponding boiling-points noted. Then, the same apparatus being used, the boiling-point of water was noted, small amounts of acetone added and readings taken. Here, however, practical difficulties made it necessary to discard the Beckmann apparatus as unsuited for this work.

As the vapor in equilibrium with dilute aqueous solutions of acetone contains a far larger percentage of acetone than does the solution, it is necessary, if one wishes to obtain a constant thermometer reading at constant pressure, that the heating must be performed very uniformly — or in other words, when this Beckmann apparatus was used, it was found possible to raise or lower the boiling-point and *keep it fairly constant at one point* by changing the rapidity of the heating. (The possibility of radiation from the source of heat was of course excluded by the use of asbestos mantles.) The larger the condensing chamber the greater were the variations observed. Moreover it was found that when the tube containing the condensed vapor dipped *below* the surface of the liquid in the boiling-flask (as is invariably shown in text-books on physicochemical methods) small explosions occurred which were due to the sudden superheating of the returned condensed vapor. This is easily understood when it is stated that in this especial case the condensed vapor frequently has a boiling-point lying twenty-five degrees ·below that of the solution with which it had been in equilibrium, and consequently

it must have a very high vapor-pressure at the temperature of the boiling solution. The Beckmann apparatus cannot therefore be used with two components which are both sensibly volatile unless special precautions are taken.

It was then decided that the most accurate readings could be made only by making use of large amounts of solution with a relative small vapor space above for the condensing chamber.

The boiling-point readings therefore were taken after adding small amounts of acetone to water in a one liter balloon flask, the condensing chamber being a long Liebig condenser. The amount of solution used was never less than 400 cc. The acetone was added through the condenser after the solution had been allowed to cool down sufficiently. Diffusion of the vapor into the air was practically prevented by the very cold surface of the condenser walls, and by having a cork fitting loosely in the top. Making use of this simple apparatus, it was very easy to obtain readings constant to tenths of degrees, whereas with the Beckmann apparatus it was not at all unusual to have readings vary whole degrees by mere variation of the rate of heating.

When the whole boiling-point curve had been determined, a third hole was made in the cork of the liter flask and through it was passed a glass tube AB, blown as shown in the figure (see Fig. 1). Its length was 18 cm, mean diameter 20 mm, capacity of bulb B up to the side opening D about 8 cc. Through the drawn-out portion of the bulb B is sealed a rather heavy platinum wire G, whose purpose is to help conduct heat from the boiling solution outside to the contents of the receiver B. In the sides of the latter are two openings D and E, the former allowing the vapor and excess of condensed vapor to return to the boiling solution, while through the latter (E) passes the glass tube which serves to catch the condensed vapor, and deliver it through a small opening at the end of the tube into the receiver B, just above the platinum wire. Above the lower end of this tube and just above G are placed, in such amount as practically to fill the bulb B, tetrahedra made either of silver, copper or platinum. Any of these, it may be remarked, are infinitely bet-

ter as a means of conveying heat than the beads, agates, etc., which are so frequently used in boiling-point determinations.[1] The thermometer which is placed in the tube AB is always in-
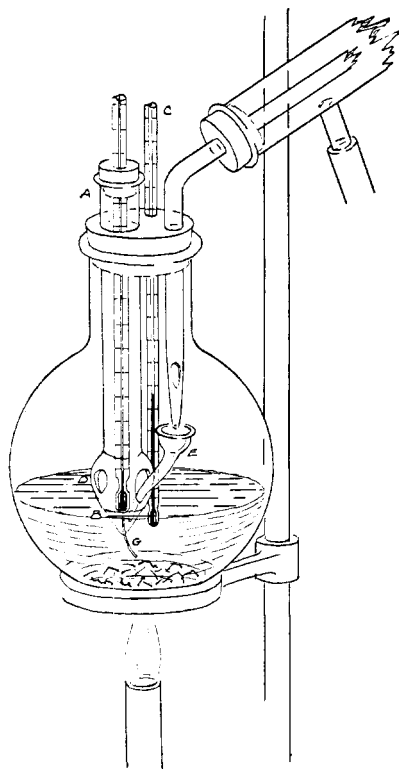

Fig. 1

serted to such an extent that no part of its bulb is as high up as the opening D.

Starting now with any solution of the two components, acetone and water, one arranges the apparatus so that one thermometer is in the solution, and the tube AB is so placed that no liquid can enter it at D and no condensed vapor can fall from the re- turn condenser into E. The solution is heated and the boiling- point noted. When several readings have shown this to be con-

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[1] Compare Beckmann. Zeit. phys. Chem. **21**, 248 (1896).

stant, the whole tube AB is turned so that the liquid from the condensing tube may keep dropping into E, and then AB is slowly lowered into the solution. The extent of this lowering must depend on different circumstances. Thus, in case there is a great difference in the boiling-points of the vapor and solution, it will often be found necessary to let only the platinum wire G come into contact with the solution in the larger flask. In case there is no great difference in the boiling-points, it may be necessary to immerse the bulb B to a considerable extent, but *never* up to the opening D. Under these circumstances the liquid in B will boil vigorously, provided that one avoids superheating by having sufficient of the tetrahedra present, and that one does not allow all of the condensed vapor to pass into the receiver B. No fixed rule can be laid down to regulate these details, a knowledge of which is acquired after a very short practice. The writer has found, however, that superheating is apt to cause more trouble than having an excess of the condensed vapor return, since the latter can be so readily checked by narrowing the receiving tube at its point of delivery above G.

When the liquid in the receiver starts to boil, it will be noticed that the reading of the thermometer immersed in it shows lower and lower temperatures, until finally it becomes constant, rarely varying $0.05°$ in an hour. This constant reading gives the boiling-temperature of the condensed vapor, whose composition may now be very readily determined from the boiling-point curve.

When a series of readings are to be made, the modus operandi is varied but slightly. First of all one determines whether one of the pure components gives a vapor whose boiling-point is the same as that of the component. If the liquid be absolutely pure this must be the case. If it is not, there may be a slight variation. With the apparatus described in this paper, it has not been found possible to have the returned vapor in the inner tube boil vigorously unless there was a difference of about one degree in the boiling-points of the two liquids. The heat supplied from the outer liquid must be sufficient to heat up the returned

vapor to its boiling-point and vaporize some of it. The conduction of the heat must therefore be very rapid if the condensed vapor is returned rapidly, and it is very doubtful therefore if glass is the best material for the construction of the bulb B when dilute solutions are being used. Experiments are being made with a silver receiver to ascertain if it is not possible to have vigorous ebullition in the inner tube when there is but a very slight difference in the boiling-points of liquid and vapor. Such a result can undoubtedly be obtained by varying the size of the apparatus and introducing electric heating of the inner tube, but it is hoped that a more simple form of apparatus may prove satisfactory. With such a device one could ascertain the purity of a substance by the boiling-point method very quickly. The advantage of this over the ordinary method would be that variations of pressure during the operation could be completely ignored.

After the preliminary determination, the other component is added in small known amounts, the tube AB is lowered until both openings E and D are below the level of the solution, and the flask is heated until the readings of both thermometers show the same temperature — the boiling-point of the solution. The receiver AB is now raised and turned to catch the returned condensed vapor. This will in time completely displace the solution with which it has been filled, and soon show a constant boiling-point. One must now note also the temperature of the boiling liquid outside. It will sometimes show a rise of 0.05° to 0.10°. It is from the extent of this rise that corrections, if required, must be calculated. After these boiling-points have been determined, the bulb is again totally immersed in the solution when both thermometers must again show the original readings. It will be seen that, by working in this manner, a continuous series of readings may be made quickly, the boiling-curve of the solutions and that of the vapor being determined at the same time. This is the method which was used in the case of benzene and carbon bisulfide and is decidedly more expeditious than the one previously described for the case of acetone

and water, where the boiling-point curves are determined separately.

The very important question in connection with this work which presented itself at the outset was "Does the presence of the great volume of solution boiling at a far higher temperature influence the reading of the thermometer in the tube AB?" If this does have any effect, it will render the method useless in so far as its claim as a method of analysis is concerned. But continued observations showed that, when the liquid in the bulb was boiling regularly, neither immersion almost to the opening D nor raising until the point G just touched the surface of the liquid, caused an appreciable (i. e. up to 0.02°) variation in the reading. This cannot be said of the preliminary measurements, as the writer had then to overcome the difficulties due to superheating, crude form of apparatus, etc. The inner boiling-tube described in this paper has been selected only after experiments had been tried with scores of others of different sizes and shapes. The constancy of the readings as finally obtained from the apparatus in its present form forces one to the conclusion that the ebullition of the liquid around the thermometer in B cuts off all heat effects due to the proximity of the outer solution, and that this thermometer can indicate a temperature none other than that of the liquid boiling in the bulb B.

The temperature measurements were made with two 100° thermometers divided into tenths of degrees. These were carefully compared with a Reichsanstalt, and all readings given are corrected. The pressures as given in the first two tables are not corrected, since the corrections as applied would be small in proportion to other errors present in the method in its first application. In the tables V, VI, and VII the pressures given are corrected.

The first table contains the data for the boiling-point curve for acetone and water. Column I shows the percentage in grams of acetone in the solution, Column II the boiling-point of this solution, Column III the barometric pressure at the time the boiling-point was taken. The determinations were not all made on the same day.

TABLE I

I % Acetone	II B Pt	III Bar	I % Acetone	II B Pt	III Bar
100.0	56.15°	748.4	23.61	68.95	736.6
95.29	57.22	748.4	18.90	71.90	740.0
89.19	58.33	748.2	17.21	73.31	740.3
84.65	58.99	738.9			
77.79	59.74	748.6	16.49	73.56	739.5
72.07	60.45	748.6	12.46	77.16	740.0
65.86	61.02	748.7	9.58	80.70	739.6
54.74	62.08	748.4	4.56	88.70	739.5
46.71	63.23	741.8	1.9	94.63	740.1
35.90	65.91	741.6	0.0	99.26	740.2

The next table shows the boiling-points of the condensed vapors as compared with those of the solutions with which they are in equilibrium. At once the question arises : — how do the determinations made in this manner compare with those found by other methods? In answering this, the writer made use of the still-head method proposed by Brown[1] in order to obtain and analyze the vapor given off by a solution at a given temperature.

The method rests on the principle that the composition of a vapor issuing freely from an opening depends on the temperature of the surrounding walls. If the temperature be higher than that at which the substance vaporizes, the vapor will pass on unchanged in composition. If the temperature be lower than that of the vapor passing into the worm of the still-head, condensation either total or partial will take place, and whatever vapor escapes from the top of the coil will have the same composition as if it had been removed directly from a solution boiling at that temperature. The temperature of the vapor in the still-head and not the boiling-temperature of the solution in the still-head determines therefore the composition of the issuing vapor, so long as the still-head temperature is not higher than that of the boiling solution.

The advantage of using this method should lie in the fact that the only precautions necessary in its use are that all the vapor should be condensed after its removal from the worm, and

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[1] Brown. Jour. Chem. Soc. **39**, 517 (1881).

that the temperature of the issuing vapor should be constant. In the measurements recorded below, these details have been properly attended to.

In this table of comparison (Table II), the first column shows the boiling-point of the acetone in the outer flask, or the temperature of the still-head (these latter measurements being marked with an asterisk); the second column shows the boiling-point of the condensed vapor in the tube B, or the boiling-point of the distillate from the still-head (also marked with an asterisk); the third column the pressures, which are not corrected.

TABLE II

I B Pt solution	II B Pt vapor	III Bar	I B Pt solution	II B Pt vapor	III Bar
62.45°	57.4°	745	82.1°	60.2°	736
63.6	57.9	745	82.55	60.35	735
*65.5	*57.4	733	82.60	60.28	735
65.75	58.0	741	84.15	60.52	735
*67.0	*57.75	733	85.0	60.6	735
68.3	58.6	740	88.0	61.43	735
*69.0	*58.4	733	*90.0	*61.90	732
70.85	59.0	741	90.4	62.0	734
71.9	59.15	740	*91.4	*63.60	728
*73.0	*59.2	734	92.0	64.55	734
73.8	59.25	738	94.1	65.05	735
75.8	59.48	738	*94.0	*65.90	728
77.15	59.7	737	94.5	66.90	735
78.9	59.95	737	95.3	68.3	735
*80.5	*59.8	731			

The data of Tables I and II are represented graphically in Fig. 2,[1] the curves being plotted in the ordinary manner. For example a solution of boiling-point X returns to the bulb B a liquid whose boiling-point lies at Y. The point Z on the vapor composition curve is thus determined.

The results obtained by the different methods agree quite well, but in almost all cases the still-head method shows more acetone present in the distillate than is found by the other method, the maximum difference being slightly over one per-

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[1] It is probable that the waviness in the lower end of the curve does not represent the facts as a smooth curve would have done.
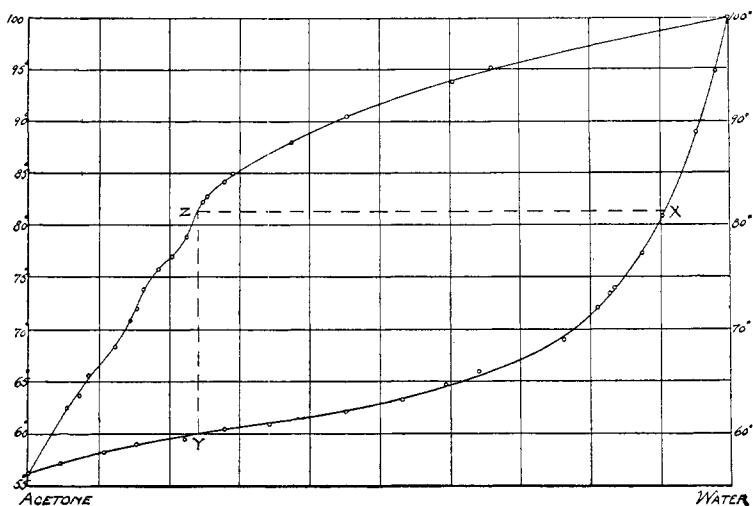
Fig. 2

cent. The uniform variation in the one direction may be explained in one of two ways:

(1) In the returned-vapor method, it is possible that the vapor, descending, is deprived of some of its more volatile component before it reaches the tube B, and if this proceeds uniformly the boiling-point will be constant, and give a higher reading than it should.

(2) In the constant still-head method as used by the writer, some error is present which allows more of the more volatile component to pass over than corresponds to the true composition of the vapor.

Owing to the small differences observed in the results from the two methods when acetone and water were used, it was thought advisable to further test the method by a case which had been examined by another investigator,[1] where preliminary measurements showed the probability of considerable difference. The components were benzene and carbon bisulfide. Considerable care was taken to obtain these substances pure. The benzene was first fractionated, then shaken repeatedly with concentrated sulfuric acid, crystallized out and again subjected to

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[1] Brown. Jour. Chem. Soc. **35**, 547 (1879).

fractional distillation. The carbon bisulfide was shaken with sulfuric acid, mercurous sulfate, then with mercury and finally fractionated over lime.

The results obtained by our own apparatus are given in Table III. In columns I and II are given the percentages (always in grams) of the carbon bisulfide and benzene which correspond to the boiling-points given in column III, the barometric pressure being shown in column IV. In the last column are given the boiling-points of the condensed vapors corresponding to the respective solutions.

TABLE III

I % Acetone	II % Benzene	III B Pt solution	IV Bar	V B Pt vapor
0.00	100.00	79.58	738.8	79.54
3.04	96.96	77.07	737.9	73.70
8.61	91.39	73.48	737.4	66.65
18.11	81.89	68.17	739.3	60.25
25.74	74.26	64.56	739.3	56.80
31.88	68.12	62.02	739.3	54.38
40.45	59.55	58.90	739.4	62.30
49.66	50.34	56.32	742.4	51.35
55.21	44.79	54.70	742.4	50.45
58.56	41.44	53.85	742.5	50.10
64.57	35.43	52.40	742.5	49.20
73.01	26.99	50.70	742.6	48.25
79.47	20.53	49.38	742.6	47.75
87.29	12.71	47.93	744.0	47.00
100.00	0.00	45.82	744.1	45.75

When the data obtained above are plotted and compared with the results given by Brown[1] in his final table, it is found that they do not agree. The reason is not far to seek. Brown determined his boiling-point curve, not by measurement of the boiling-temperature of solutions of known concentration, but from the composition of the vapor he calculated the composition of the solution remaining in the flask, and gave this boiling-point as being for this concentration. Any error in the vapor analysis would at once show itself in the boiling-point curve. If his

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[1] Brown. Ibid, **35**, 561 (1879).

method were perfectly reliable, if at any time he could determine accurately the composition and amount of the vapor condensed, his boiling-points should be perfectly accurate and agree with each other. That this is the case cannot be said.

In the following table there are collected the data given in Brown's tables numbered II, V, VIII, XI, XII and XVII, no essential ones being omitted. In the first column is given the molecular percentage of carbon bisulfide in the solution, this being determined as above stated. In the second column is given the boiling-point corresponding to this composition. The first measurement in each table represents the first distillation performed.

TABLE IV

% CS₂	B Pt	% CS₂	B Pt	% CS₂	B Pt
Table II $p=772$		Table V $p=763$		Table VIII $p=757$	
....	....	....	....	70.86	51.00
61.95	52.5	61.76	52.0	61.81	52.90
44.80	58.0	44.50	58.0	Table XI $p=750$	
....	....	....	....	40.8	56.0
38.60	60.0	38.80	60.0	38.64	59.0
25.86	66.0	25.81	66.0	25.91	63.8
....	....	....	....	Table XIV $p=752$	
19.59	70.0	18.96	70.0	18.33	66.2
....	....	Table XVII		....	....
....	....	9.44	70.6	9.69	72.4

Solutions having the compositions of 61.8 percent carbon bisulfide have given as their respective boiling-points, 52.5°, 52.0° and 52.9°; with 38.6 percent of carbon bisulfide, the boiling-points are 60.0°, 60.0° and 59.0°; with 25.8 percent, 66.0°, 66.0° and 63.8°; with 19 percent approximately, these boiling-points are 70.0°, 70.0° and 66.2°; with 9.44 and 9.69 percent the boiling-points are 70.6° and 72.4°. With the single exception of the first case, it will be noted that the boiling-point of a solution made up in definite amounts is lower than that which would be calculated from the composition of the vapor. This must mean that the method which was used kept taking away a greater percentage of the more volatile component than actually exists in the vapor.

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With the view of still further testing the agreement of the results obtained by distillation, the writer has rearranged those of Brown's tables which are numbered I, IV, VII, X, XIV, and XVI. In the first column of Table V will be found the mean boiling-point at which distillation was effected; in the second is given the vapor composition expressed in molecular percentage of carbon bisulfide. From the mean boiling-points it is impos-

TABLE V

I	II	I	II	I	II
Mean B Pt	Vapor composition	Mean B Pt	Vapor composition	Mean B Pt	Vapor composition
Table I		Table IV		Table VII	
....	....	....	....	51.1	88.27
53.25	82.94	53.00	84.26	53.10	83.37
54.50	81.24	54.50	82.45	....	....
57.00	75.36	57.25	76.24	Table X	
59.00	70.26	59.00	72.48	59.3	68.35
61.50	64.05	61.50	66.67	61.4	63.21
64.50	56.44	64.50	59.14	64.3	55.46
....	....	....	....	Table XVII	
....	....	....	....	67.2	47.88
68.00	45.76	68.00	49.56	68.57	43.55
....	....	....	....	71.75	33.47
....	....	....	....	Table XVI	
....	....	....	....	71.6	29.50
72.50	30.56	72.50	33.85	73.2	24.36
76.50	15.05	76.92	16.27	76.45	11.80

sible by a consideration of this table to ascribe to the determination of the vapor composition any great accuracy. Variations are present ranging from one-half to nine percent so that it is absolutely impossible to use the data obtained by Brown in proof of a thermodynamic formula.[1]

From the consideration of Table IV it follows that the curve showing vapor compositions (Brown's results) is displaced toward the side of the more volatile component, and since it is in this direction that this curve departs from the one constructed from the data given in Table III, it is necessary to find where the error is present.

[1] Compare Lehfeldt. Phil. Mag. [5] 40, 398 (1895).

The sources of probable error have been mentioned in the consideration of the discrepancies in the determinations for acetone and water.   Of these the first one which will be considered is that due to the still-head.   Very careful experiments were now made to see if any other precaution in obtaining a distillate of constant composition were necessary beside that of maintaining a constant temperature in the still-head itself.   It was found that the writer had overlooked possible condensation in the adapter which connects the still to the worm of the still-head. In the acetone-water distillation by the still-head method this adapter was very short, and of considerable diameter and was surrounded by asbestos.   In the benzene carbon bisulfide distillation, an adapter fifteen centimeters long was used, and it also was covered by asbestos.   Nevertheless condensation occurred in it, and this rendered the method useless as a method of comparison.

Since the results obtained by Brown when he used the still-head agreed with those he had previously determined by direct distillation, and since it has been demonstrated in Tables IV and V that these results do not agree very well with each other, it is necessary to obtain results by some other method if a just comparison is to be made.   Moreover there is the possibility that the benzene used by Brown may have contained thiophene, whose effect cannot be stated.

For this purpose a one litre balloon flask was fitted with a cork through which passed a thermometer and a tube leading to a Liebig condenser.   The neck of this tube was heated up to and beyond the bend by an electric coil, which was again surrounded by asbestos.   This prevents all condensation of the vapor before it passes into the condensing tube.   From this condenser it flows into a receiver which holds about 35 cc and from which it could be drawn off by means of a stop-cock. This receiver has attached to it a glass arm which allows of communication with the air outside by means of a small opening at the side.   In this way one is sure that if the distillation be carried on moderately, the condensation should be almost perfect, but it is very doubtful if complete condensation were

attained. The observations necessary are initial and final boil-
ing-points of the solution which is being distilled, boiling-point
of the distillate and the corresponding barometric pressures.

In Table VI are given the results obtained with carbon
bisulfide and benzene; in column I the initial and final boiling-
points, in II the mean of these readings. Column III contains the
boiling-point of the distillate, and IV the corresponding pressures.

TABLE VI

I Boiling- points Initial Final	II Mean B Pt	III B Pt vapor	IV Bar	I Boiling- points Initial Final	II Mean B Pt	III B Pt vapor	IV Bar
48.1–48.5	48.3	47.25	737.9	64.1–64.9	64.5	55.85	751.8
48.5–49.0	48.75	47.30	736.8	64.9–65.7	65.3	56.55	751.7
49.0–50.1	49.55	47.55	736.3	65.7–66.5	66.1	57.50	751.7
50.1–50.7	50.4	48.00	732.0	66.5–67.6	67.05	58.10	751.7
51.1–51.8	51.45	48.30	735.5	67.6–68.6	68.1	59.35	751.5
51.8–52.6	52.2	48.96	735.1	68.7–69.8	69.25	59.31	743.8
52.6–53.7	53.15	49.42	735.6	69.8–71.0	70.4	60.52	743.7
53.7–55.6	54.65	49.80	735.7	71.0–72.2	71.6	62.75	743.5
55.6–58.5	57.05	50.80	735.8	72.2–73.5	72.85	64.62	743.4
58.8–59.1	58.85	52.05	751.6	73.8–75.0	74.4	66.71	743.2
59.1–59.6	59.35	52.65	751.6	73.0–75.9	75.45	68.58	743.0
59.6–60.1	59.85	53.04	751.5	76.3–77.0	76.35	71.60	742.8
60.1–60.9	60.5	53.41	751.4	77.0–77.8	77.4	74.58	742.6
60.9–61.7	61.3	53.55	751.4	77.8–78.4	78.1	75.35	742.5
61.7–62.6	62.15	54.08	751.4	78.4–78.9	78.65	77.42	742.3
62.6–63.4	63.0	54.62	751.5				

When the results given in the table are plotted and com-
pared with those of Table III, it is seen that the two methods do
not give concordant results. If one assumes that the distillation
method used in the comparison gives results which are approxi-
mately correct — which assumption appears very reasonable —
it is certain that the other method is not accurate. But the
variations are again in the same direction as before — the boil-
ing-points of the vapor as determined by this especial apparatus
are all of them too high. As it has been shown previously that
this could not be due to radiation, it must mean that not all of
the more volatile component is returned to the tube B. If the
condensed vapor flowing back into the flask comes into contact

with the ascending vapor of which the temperature is considerably higher, it seems not unreasonable to suppose that the ascending vapor might take along with it from this liquid some of the more volatile component so that the liquid which actually drops into the bulb B has not the actual composition of the vapor. Moreover it seems not impossible that, if the heating be performed regularly, the boiling-point of this returned liquid might remain perfectly constant.

In order to examine this possibility the writer has altered the form of the condensing tube. In place of having the vapor sweep continuously along a considerable length of the condensing tube which is wetted by the returning liquid, the vapor enters this tube through a hole near the cork. The actual condensation takes place as close as possible to the flask which contains the boiling solution. The returning vapor drops to the lower part of the condensing tube which is drawn out to a point, and from this it falls into the bulb B. In Fig. 1 is shown the apparatus in the form finally used.
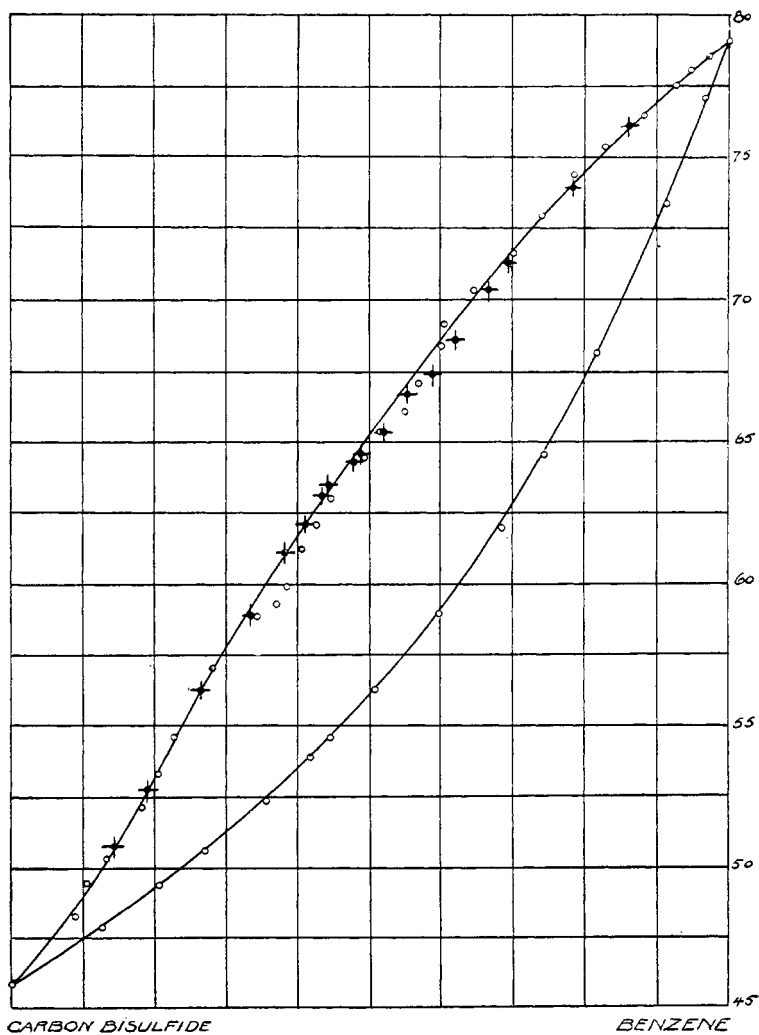
The following table gives in column I the boiling-point of the solution in the outer flask ; in column II the corresponding boiling-point of the condensed vapor in tube B; in column III the pressures at which these measurements were taken.

TABLE VII

I B Pt solu- tion	II B Pt vapor	III Bar	I B Pt solu- tion	II B Pt vapor	III Bar
50.70	48.25	739.5	64.80	56.14	739.6
52.46	49.04	739.4	65.38	56.74	739.7
56.15	50.52	739.4	66.60	57.75	739.7
58.91	52.01	739.4	66.70	57.80	739.6
61.20	52.82	730.2	67.33	58.68	739.6
62.28	53.91	729.8	68.58	59.81	739.6
63.19	54.26	729.4	70.30	61.28	739.5
63.48	54.70	729.1	71.30	62.55	739.4
64.02	55.48	739.7	73.90	66.51	739.4
64.24	55.68	739.7	76.00	70.52	739.3
64.30	55.76	739.7			

When the results given in Table VII are plotted and compared with those given by the distillation method (Table VI) it

will be found that the curves of vapor composition coincide very well. In Fig. 3[1] the determinations given in Table VI are represented by a dot, while those of Table VII are represented by a cross. The variations of the former from the probable curve

CARBON BISULFIDE   BENZENE

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[1] No attempt has been made to correct for the varying pressures, so that the curves are really only approximations.

seem to be greater than those of the latter, and are undoubtedly due to the loss of carbon bisulfide in the distillation, although considerable care was taken to avoid this almost certain source of error by keeping the condenser at about 3°. Moreover, the fact that the boiling-points as determined by the returned-vapor method lie *lower* than those found by the distillation method gives a strong support to this conclusion.

The fair agreement between the results as given by the two different methods shows that at least one source of error in the original apparatus has been detected and almost entirely overcome. While it is apparent that *absolute* accuracy (in this instance the error is probably not greater than $\pm$ 1 percent) may hardly be attained owing to the action of the ascending vapors on the descending liquid, still the results prove the method as reliable, in this case at least, as the method of distillation. In the latter it is necessary to determine the *mean* boiling-point of a solution which gives off a certain amount of distillate for analysis. Moreover the pressure variations have to be regarded in a very careful way and this in actual work complicates the experiment to a considerable extent. In the method described in this paper both boiling-points are determined simultaneously under the same pressure, and the rapidity of the operation is such that a complete determination of the vapor-solution curve may be readily carried out in one day.

Of course if one wishes to work under pressures different from atmospheric, the apparatus will require modification. Here the necessity of excluding all possibility of leakage will require that the part of the inner tube which passes through the cork shall be immovable. It would then be necessary to have the tube made of two parts, the lower being capable of adjustment from without. This may possibly be effected by fitting permanently into the inner tube a piece of steel which being acted on by a magnet from without can allow of the lower portion B being raised or lowered at will. In such cases as this, it may be questionable whether this method is as rapid as the ordinary distillation method.

If the application of this method of vapor analysis were confined to two-component systems where both components are volatile, it would appear as if the field where it might be used was very limited ; but such is not the case.   The composition of the vapor phase in equilibrium with any solution containing two volatile and any number of non-volatile components may be readily examined by this method.   Systems of this kind have of late been made a subject of study by Miller[1] who has shown by use of the Gibbs energy theory the intimate connection existing between solubility and partial vapor-pressures.   When the bearing of the demonstration given by Miller — that it is always possible by a correct choice of the third (non-volatile) component to change the relative partial pressures of the two volatile components and hence render their separation by fractional distillation more easy — is fully appreciated, the work of the organic technical chemist will be performed on a far more intelligent basis.   For instance, in the case of acetone and water, it is apparent from the relation deduced by Miller that the addition of sodium chlorid or any other non-volatile substance more soluble in water than in acetone will displace the curve of vapor composition more to the acetone side.   So also in all cases where maxima or minima boiling-points occur, that is in all cases where complete fractional separation of the components by the usual operations is impossible, the displacement of the relation between the partial pressures of the two volatile components may probably be readily effected by the choice of a third whose solubilities in the two volatile components is widely different.   In any of these cases the comparative value of the different salts in changing the partial pressures may be easily tested by the use of the apparatus described in this paper.

The relation of the curves representing vapor and solution phases under varying pressure has not, so far as the writer is aware, been made the subject of an experimental study, with the exception of one isolated case.   In this case Brown[2] studied the relative composition of vapor and solution phases under the

[1] Jour. Phys. Chem. 1, 633 (1897).
[2] Jour. Chem. Soc. 39, 304 (1881).

pressures of 760 mm and 430 mm and came to the conclusion that the pressure term does not appear as a factor in the equilibrium. When his results are plotted in the manner used in this paper, it seems as if the relative positions of the curves were displaced in such a way that decrease of pressure caused the vapor and solution curves to approach each other; but the lack of experimental data prevents the drawing of definite conclusions on this point. The subject is of importance since it deals with the question whether the effectiveness of a fractional distillation attains its maximum under increased or under reduced pressure.

If the vapor composition be accurately determined one may readily calculate the partial pressures of the several components if the assumptions be made that Henry's law holds and that each component exists in the vapor in its normal state. From the partial pressures, especially those for dilute solutions, the molecular weight of the dissolved substance may be calculated from the van 't Hoff-Raoult formula. It is expected that the calculation of these pressures and the comparison of other relations may form the basis for a subsequent paper when measurements on the vapor-pressures of acetone-water mixtures shall have been completed.

In the present paper has been given:

1. The description and preliminary tests of an apparatus for rapid vapor analysis.

2. Its advantages and probable errors.

3. The objections which are to be raised against the employment of the Beckmann boiling-point apparatus when both components are volatile.

4. A new method of determining the purity of an organic compound by means of boiling-point comparisons.

5. Comments on the maximum effectiveness of fractional distillation.

6. The advantages and a possible error in the use of Brown's constant temperature still-head.

To Professor Bancroft at whose suggestions and under whose direction this subject has been examined, the writer expresses his thanks.

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