

LXXVI.—*Fractional Distillation as a Method of Quantitative Analysis.*

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IN a paper by one of us entitled "Experiments on Fractional Distillation" (*J. Soc. Chem. Ind.*, 1900, 19, 1072), it was pointed out that the composition of a mixture of homologous substances could in many cases be ascertained with a fair degree of accuracy from the results of two or three fractional distillations with an efficient still-head, or in the case of a mixture of two components which are not difficult to separate, from the result of a single distillation.

The method depends on the following facts:—Taking first the simplest case, that of a mixture of two liquids, it is found that the weight of distillate which comes over below the middle point* is almost exactly equal to that of the component of lower boiling point, even when the separation is very far from complete.

If the original mixture contains more than two, say n , components, the weights of these components will be very nearly equal respectively to (1) the weight of distillate below the first middle point, (2 to $n - 1$) the

* By middle point is to be understood the temperature midway between the boiling points of the two liquids, whether pure substances or mixtures of constant boiling point, into which the original mixture tends to separate; or, in the case of a more complex mixture, the temperature midway between the boiling points of any two consecutive fractions of constant boiling point.

weights of distillate between the successive middle points, (n) the weight above the last middle point.

Only two mixtures of substances which are not homologous—methyl alcohol-water and *isoamyl* alcohol-benzene—and which separate normally into the two components, have been examined, but a considerable number of cases in which mixtures of minimum boiling point are formed have been investigated, and it has been found that such mixtures of constant boiling point behave like pure liquids. Thus, if the composition of the mixture of minimum boiling point is known, that of the original mixture may be calculated from the weight of distillate below the middle point, and, on the other hand, if the composition of the original mixture is known, that of the mixture of minimum boiling point may be calculated. The same remarks would apply to binary mixtures of maximum boiling point, such as that of formic acid and water, but so far we have not examined any such mixture.

It is obvious that there must be some loss of liquid by evaporation, which makes the weight of distillate somewhat too low. This loss will be greater as the initial boiling point is lower, and as the temperature of the room is higher. It is not proportional to the amount of liquid distilled, for a great part of the loss is caused by the saturation of the air in the flask and still-head while it is being expelled by the rising vapour. Under otherwise similar conditions, the loss is therefore roughly proportional to the volume of air in the still and still-head, that it is advantageous to use as small a flask as possible and to employ a still-head of as small capacity as is consistent with efficiency. A plain, wide still-head or one with spherical bulbs is the least satisfactory, but the "pear" still-head, owing to the diminished capacity of the bulbs and the increased efficiency, gives much better results. Of all forms, the "evaporator" still-head is the best, because the capacity is relatively small, and the amount of condensed liquid in it is smaller than in any other of equal efficiency, and because almost the whole of the liquid returns to the still at the end of the distillation.

With a liquid of low viscosity, like one of the paraffins, the quantity of liquid left in the still-head is almost inappreciable, and in other cases it may be reduced to a very small amount by disconnecting the apparatus while still hot from the condenser, shaking out any liquid remaining in the funnels, and tilting the tube from side to side to facilitate the flow of the residual liquid back to the still.*

When the liquid left at the end of the distillation was *n*-hexane, hardly a trace was visible in the still-head after cooling, even when left

* In a new form of "evaporator" still-head, which will be described later, the little funnels are done away with, and the tube merely requires to be tilted while still hot.

in position, whilst with benzene as the final liquid, the amount could certainly be reduced to 0.1 gram by taking down the still-head while hot, as described.

For these reasons, the "evaporator" still-head was used for all determinations, except when ethyl alcohol, benzene and water, ethyl alcohol and hexane, or ethyl alcohol and water were distilled together.

As an example of the estimation of loss by evaporation, we may cite the distillation of mixtures of methyl alcohol and benzene, one with benzene, the other with methyl alcohol in excess over the amount present in the mixture of constant boiling point.

In each case, the distillation was stopped when the middle point was reached, and the liquid left in the still after cooling was weighed.

The results obtained were as follows :

	Benzene in excess.	Alcohol in excess.
Weight of distillate	128.7	132.0
Weight of liquid in still	24.9	27.2
Total.....	153.6	159.2
Weight of mixture taken	154.2	160.1
Loss by evaporation and in still-head ...	0.6	0.9

When the benzene was in excess it is quite certain that the weight of it left in the still-head was not greater than 0.1 gram, and the loss by evaporation was therefore taken to be 0.5 gram, and in the calculation of composition this amount was added to the observed weight of distillate.

Allowing the same amount, 0.5 gram, for loss by evaporation in the second distillation, that would leave 0.4 gram as the weight of liquid—mostly methyl alcohol—in the still-head, an amount which appears quite reasonable, for this more viscous liquid did not flow back nearly so freely, and there was a visibly much larger amount left in the still-head.

When the "evaporator" still-head was employed, the correction applied for loss by evaporation was usually 0.4 or 0.3 gram. With the 18-column dephlegmator, which was used for the other distillations, the loss was certainly greater, but could not be accurately estimated.

EXPERIMENTAL.

Methyl Alcohol and Water.

Two determinations were made to test the value of the method, mixtures of known composition being distilled, in one of which the alcohol, in the other the water, was in large excess.

Methyl alcohol in large excess.

Boiling points: Methyl alcohol, 64.7° ; water, 100.0° ; middle point, 82.35° .

Mixture taken.	Weight below middle point.	Percentage composition of mixture.		
		Found.		Taken.
		Uncorrected.	Corrected.	
Alcohol 90.9 Water 24.4 <hr/> 115.3	Observed 90.5 Corrected 90.8	Alcohol 78.5 Water 21.5 <hr/> 100.0	78.7 21.3 <hr/> 100.0	78.8 21.2 <hr/> 100.0

Water in large excess.

Mixture taken.	Weight below middle point.	Percentage composition of mixture.		
		Found.		Taken.
		Uncorrected.	Corrected.	
Alcohol 39.7 Water 161.5 <hr/> 201.2	Observed 33.9 Corrected 34.2	Alcohol 16.9 Water 83.1 <hr/> 100.0	17.0 83.0 <hr/> 100.0	19.7 80.3 <hr/> 100.0

This second result is apparently unsatisfactory, but it is always difficult to separate the more volatile component of a mixture when present in relatively small amount, and, in such a case, a second distillation is usually necessary. The first distillation was therefore continued until the temperature reached 100° , and the whole of the distillate, weighing 66.8 grams, was then redistilled, and the double correction for loss by evaporation was applied. The weight below the middle point was now 38.9, corrected 39.5, giving the percentage composition:

	Uncorrected.	Corrected.	Taken.
Alcohol	19.3	19.6	19.7
Water	80.7	80.4	80.3
	<hr/> 100.0	<hr/> 100.0	<hr/> 100.0

It will thus be seen that, by repeating the distillation, the result was as satisfactory as that given by a single distillation when the alcohol was

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in excess. Even without correcting for loss by evaporation, the agreement is fairly good, but it is much improved by introducing the correction.

isoAmyl Alcohol and Benzene.

Boiling points: benzene, 80.2° ; *isoamyl* alcohol, 132.05° ; middle point, 106.1° .

Mixture taken.	Weight below middle point.	Percentage composition of mixture.		
		Found.		Taken.
		Uncorrected.	Corrected.	
Alcohol 26.6 Benzene 85.7	Observed 85.55 Corrected 85.85	Alcohol 23.8 Benzene 76.2	23.6 76.4	23.7 76.3
112.3		100.0	100.0	100.0

The separation is here an easy one and the agreement is exceedingly good.

Mixtures of Constant Boiling Point.

The first two experiments serve to show that the quantity of a mixture of constant boiling point may be estimated by the distillation method in the same way as a pure substance. The methods of experiment and of calculation are similar in all respects.

For the sake of brevity, a mixture of constant boiling point of two components will be referred to in this paper as a "binary" mixture and a mixture of constant boiling point of three components as a "ternary" mixture.

isoPropyl Alcohol and Water.

Boiling points: binary mixture, 80.37° ; water, 100.0° ; middle point, 90.2° .

Mixture taken.	Weight below middle point.	Percentage composition of mixture.		
		Found.		Taken.
		Uncorrected.	Corrected.	
Binary mixture } 57.7 Water 20.1	Observed 57.3 Corrected 57.6	Binary mixture } 73.65 Water 26.35	74.05 25.95	74.15 25.85
77.8		100.00	100.00	100.00

The agreement in this case is perfectly satisfactory.

tert. Butyl Alcohol and Water.

Boiling points: binary mixture, 79.91° ; water, 100.0° ; middle point, 89.95° .

Mixture taken.	Weight below middle point.	Percentage composition of mixture.		
		Found.		Taken.
		Uncorrected.	Corrected.	
Binary mixture } 58.8	Observed 58.2	Binary mixture } 65.9	66.25	66.6
Water } 29.5	Corrected 58.5	Water } 34.1	33.75	33.4
		100.0	100.00	100.0

Here the agreement is not quite so good, but may be regarded as fairly satisfactory.

In the following experiments, the composition of the mixtures of minimum boiling point was calculated from the results of the distillations.

n-Propyl Alcohol and Water.

For this distillation, a mixture of dry *n*-propyl alcohol with water was employed.

Boiling points: binary mixture, 87.72° ; water, 100.0° ; middle point, 93.85° .

Mixture taken.	Weight below middle point.	Percentage composition of binary mixture.		
		By distillation.		From specific gravity.
		Uncorrected.	Corrected.	
Alcohol 76.6	Observed 106.4	Alcohol 72.0	71.8	71.69
Water 50.0	Corrected 106.7	Water 28.0	28.2	28.31
126.6		100.0	100.0	100.0

The calculation is based on the following considerations. If the fractionation were complete, the original mixture would separate into (1) the binary mixture containing the whole of the alcohol, (2) the excess of water. The weight of the binary mixture is given by the corrected weight of distillate below the middle point, and thus the weight of alcohol in the binary mixture and that of the binary mixture itself are ascertained.

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The statement may be made, generally, thus: The ratio of the weight of the component not in excess in the original mixture to the corrected weight of distillate is equal to the proportion of that component in the binary mixture.

Thus, in the actual distillation: Weight of alcohol = 76.6 grams; weight of binary mixture = corrected weight of distillate below middle point = 106.7 grams. Percentage of alcohol in binary mixture = $\frac{76.6 \times 100}{106.7} = 71.8$.

The determination of the composition of the binary mixture by means of the sp. gr. has already been referred to in the paper on the properties of mixtures of the lower alcohols with water.

It will be seen that the agreement is very satisfactory.

isoAmyl Alcohol and Water.

1. *Water in excess.*

Boiling points: binary mixture, 95.15°; water, 100.0°; middle point, 97.6°.

Mixture taken.	Weight below middle point.	Percentage composition of binary mixtures.	
		Uncorrected.	Corrected.
Alcohol 38.8 Water 69.5 <hr/> 108.3	Observed 76.4 Corrected 76.9*	Alcohol 50.8 Water 49.2 <hr/> 100.0	50.5 49.5 <hr/> 100.0

* The correction introduced is slightly larger than usual on account of a minute loss of vapour during the distillation.

2. *Alcohol in excess.*

Boiling points: binary mixture, 95.15°; alcohol, 132.05°; middle point, 113.6°.

Mixture taken.	Weight below middle point.	Percentage composition of binary mixture.	
		Uncorrected.	Corrected.
Alcohol 68.3 Water 42.7 <hr/> 111.0	Observed 85.65 Corrected 85.95	Alcohol 50.1 Water 49.9 <hr/> 100.0	50.3 49.7 <hr/> 100.0

The agreement between the corrected values is very satisfactory.

Methyl Alcohol and Benzene.

These determinations have already been referred to in estimating the loss by evaporation ; full details are given below :

1. *Benzene in excess.*

Boiling points : binary mixture, 58.34° ; benzene, 80.2° ; middle point, 69.25° .

Mixture taken.	Weight below middle point.	Percentage composition of binary mixture.	
		Uncorrected.	Corrected.
Alcohol 51.2 Benzene 103.0 <hr/> 154.2	Observed 128.7 Corrected 129.2	Alcohol 39.8 Benzene 60.2 <hr/> 100.0	39.6 60.4 <hr/> 100.0

2. *Methyl alcohol in excess.*

Boiling points : binary mixture, 58.34° ; methyl alcohol, 64.7° ; middle point, 61.5° .

Mixture taken.	Weight below middle point.	Percentage composition of binary mixture.	
		Uncorrected.	Corrected.
Alcohol 79.9 Benzene 80.2 <hr/> 160.1	Observed 132.0 Corrected 132.5	Alcohol 39.2 Benzene 60.8 <hr/> 100.0	39.5 60.5 <hr/> 100.0

Ethyl Alcohol and Benzene.

Only one determination was made, the benzene being in excess, but the composition of the binary mixture was also ascertained by a determination of its sp. gr. as described in the previous paper (p. 741).

Boiling points : binary mixture, 68.24° ; benzene, 80.2° ; middle point, 74.2° .

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Mixture taken.	Weight below middle point.	Percentage composition of binary mixture.		
		By distillation.		From specific gravity.
		Uncorrected.	Corrected.	
Alcohol 25.7 Benzene 78.5	Observed 78.9 Corrected 79.2	Alcohol 32.6 Benzene 67.4	32.45 67.55	32.36 67.64
104.2		100.0	100.00	100.00

Ethyl Alcohol and Hexane.

Two distillations were made, the mixture in each case containing excess of alcohol, but both the relative and actual quantities differed considerably. The 18-column dephlegmator was employed.

Boiling points: binary mixture, 58.68°; alcohol, 78.3°; middle point, 68.5°.

Mixture taken.	Weight below middle point.	Composition of binary mixture.	
		Uncorrected.	Corrected.
I. Alcohol 127.7 Hexane 128.4	Observed 161.1 Corrected 162.1	Alcohol 20.3 Hexane 79.7	20.8 79.2
256.1		100.0	100.0
II. Alcohol 72.5 Hexane 42.0	Observed 52.8 Corrected 53.4	Alcohol 20.5 Hexane 79.5	21.3 78.7
114.5		100.0	100.0

The agreement between the two corrected values is fairly satisfactory; the percentage of alcohol was taken to be 21.0.

n-Propyl Alcohol and Benzene.

In this case, two distillations were carried out, one of a mixture with benzene in excess, the other with alcohol in excess.

1. *Benzene in excess.*

Boiling points: binary mixture, 77.12°; benzene, 80.2°; middle point, 78.65°.

2. *Alcohol in excess.*

Boiling points : binary mixture, 77.12° ; alcohol, 97.19° ; middle point, 87.15° .

Mixture taken.	Weight below middle point.	Percentage composition of binary mixture.	
		Uncorrected.	Corrected.
<i>Benzene in excess.</i>			
Alcohol 26.95	Observed 158.8	Alcohol 17.0	16.95
Benzene 163.25	Corrected 159.2	Benzene 83.0	83.05
190.2		100.0	100.00
<i>Alcohol in excess.</i>			
Alcohol 40.2	Observed 96.0	Alcohol 16.7	16.95
Benzene 80.0	Corrected 96.3	Benzene 83.3	83.05
120.2		100.0	100.00

Here there is perfect agreement between the two corrected values.

Composition of a Ternary Mixture.

When a mixture of three liquids gives rise, on distillation, to the formation of a ternary mixture of minimum boiling point, the separation may, theoretically, take place in twelve different ways, and, in addition to these, if the original mixture had the same composition as the ternary mixture, its behaviour on distillation would be precisely that of a pure liquid.

Determinations were actually made with only one set of three liquids, and we may take this case, that of a mixture of ethyl alcohol, benzene, and water, as a typical one. For the sake of convenience, we will use the initial letters, A, B, and W, to represent the three components.

The possible cases are as follows :

	First fraction.	Second fraction.	Residue.
1.	A.B.W	A.W	W
2.	„	B.W	W
3.	„	A.W	A
4.	„	A.B	A

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	First fraction.	Second fraction.	Residue.
5.	A.B.W	B.W	B
6.	„	A.B	B
7.	„	—	A
8.	„	—	B
9.	„	—	W
10.	„	—	A.B
11.	„	—	A.W
12.	„	—	B.W
13.	„	—	—

The first six cases, and, on redistillation of the first fraction, the last, would be those commonly met with. For cases 7, 8, and 9, the relative quantities of two of the liquids would have to be precisely the same as in the ternary mixture, the third liquid being in excess. With regard to cases 10, 11, and 12, the composition of the original mixture would have to be exactly such as would be obtained by mixing together the pure ternary mixture with any one of the three pure binary mixtures, although, of course, any proportion of these two mixtures might be taken. Even if these conditions as regards cases 7 to 12 were fulfilled, it is doubtful whether, owing to imperfect separation, the results specified in the above table would be actually attained, but the matter has not been examined experimentally.

Of the first six cases, the third, when ethyl alcohol is employed, is unrealisable in practice, owing to the very small difference between the boiling points of the second fraction (A.W) and the residue (A).

Mixtures, however, tending to separate in the other five ways specified, were employed for the determination of the composition of the ternary mixture.

In order to calculate this, it is necessary to know, not only the composition of the original mixtures, but also that of the binary mixture forming the second fraction. The composition of each of the three binary mixtures is now known, and, for convenience of reference, the boiling points of all possible fractions, and the percentage composition of the binary mixtures, are given below :

	Boiling points.	Percentage composition.		
		A.	B.	W.
W.	100.0°	—	—	100
B.	80.2	—	100	—
A.	78.3	100	—	—
A.W.	78.15	95.57	—	4.43
B.W.	69.25	—	91.17	8.83
A.B.	68.24	32.36	67.64	—
A.B.W.	64.86			

In making up the original mixture, the materials employed were (1) 99.5 per cent. (by weight) alcohol, (2) pure benzene, (3) pure water, (4) the binary A.B. mixture.

I.

Fractions: A.B.W.; A.W.; W. Middle points 71.53° and 89.1° .

Mixture taken.	Weights below middle points.		Composition of ternary mixture.	
	Observed.	Corrected.	Uncorrected.	Corrected.
A. 66.0 B. 74.2 W. 50.5 <hr/> 190.7	(1) 99.5 (2) 51.7	99.9 51.8	A. 16.7 B. 74.6 W. 8.7 <hr/> 100.0	16.5 74.3 9.2 <hr/> 100.0

In making the calculation, it is assumed, as before, that the corrected weights of the two distillates are equal to those of the ternary and binary mixtures respectively, which would be obtained if the separation were perfect.

That being so, in the above case, the weight of benzene in the ternary mixture is simply that of the benzene taken; the weight of alcohol in the ternary mixture is the weight taken less that in the binary mixture, which can be calculated; the weight of water is given by difference.

II *a* and II *b*.

Two mixtures were distilled in this case.

Fractions: A.B.W.; W.B.; W. Middle points 67.05° and 84.6° .

Mixture taken.	Weights below middle points.		Composition of ternary mixture.	
	Observed.	Corrected.	Uncorrected.	Corrected.
II <i>a</i> .				
A. 18.4 B. 120.0 W. 52.1 <hr/> 190.5	(1) 94.9 (2) 54.0	95.3 54.1	A. 19.4 B. 74.6 W. 6.0 <hr/> 100.0	19.3 74.2 6.5 <hr/> 100.0

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Mixture taken.	Weights below middle point.		Composition of ternary mixture.	
	Observed.	Corrected.	Uncorrected.	Corrected.
	III.			
A. 18.5 B. 90.0 W. 54.3 <hr/> 162.8	(1) 95.3 (2) 20.7	95.7 20.8	A. 19.4 B. 74.6 W. 6.0 <hr/> 100.0	19.3 74.3 6.4 <hr/> 100.0

The agreement between the two results, notwithstanding the different relative quantities in the original mixture, is remarkable.

IV. Fractions: A.B.W. ; A.B. ; A. Middle points 66.55° and 73.3°

V. „ A.B.W. ; B.W ; B. „ 67.05 „ 74.7

VI. „ A.B.W. ; A.B. ; B. „ 66.55 „ 74.2

Mixture taken.	Weight below middle point.		Composition of ternary mixture.	
	Observed.	Corrected.	Uncorrected.	Corrected.
	IV.			
A. 75.0 B. 108.0 W. 7.5 <hr/> 190.5	(1). 100.6 (2). 47.5	101.0 47.6	A. 17.1 B. 75.4 W. 7.5 <hr/> 100.0	17.5 75.1 7.4 <hr/> 100.0
	V.			
A. 18.5 B. 160.1 W. 12.1 <hr/> 190.7	(1). 97.1 (2). 52.5	97.5 52.6	A. 19.1 B. 78.2 W. 7.7 <hr/> 100.0	19.0 78.4 7.6 <hr/> 100.0

Mixture taken.	Weight below middle point.		Composition of ternary mixture.	
	Observed.	Corrected.	Uncorrected.	Corrected.
VI.				
A. 35.0 B. 148.3 W. 7.6 <hr/> 190.9	(1). 111.6 (2). 42.6	112.0 42.7	A. 19.0 B. 74.2 W. 6.8 <hr/> 100.0	18.9 74.3 6.8 <hr/> 100.0

The composition of the ternary mixture was directly determined, as described in the previous paper. The results of this determination and the mean of the results obtained by distillation, taking IIa and IIb as a single determination, are given below :

	Direct determination.	By distillation	
		uncorrected.	corrected.
Alcohol	18.5	18.3	18.2
Benzene.....	74.1	74.4	74.3
Water	7.4	7.3	7.5
	<hr/> 100.0	<hr/> 100.0	<hr/> 100.0

The agreement may be regarded as extremely satisfactory, although some of the individual values, especially those of alcohol and water in I, differ somewhat widely from the means. The explanation of the rather large errors in the first distillation is given on p. 767.

Cases to which the Distillation Method is inapplicable.

Of the numerous mixtures investigated, two only, *n*-hexane-benzene and ethyl alcohol-water, have given unsatisfactory results.

The relation of boiling point to molecular composition is very similar for both these mixtures ; in both cases, the addition of moderate quantities of the less volatile component has very slight effect on the boiling point, but whereas with ethyl alcohol and water there is undoubtedly a definite mixture of minimum boiling point, the experimental results do not indicate with certainty whether benzene and *n*-hexane behave in this way, although it is extremely probable that such a mixture, boiling less than 0.05° lower than *n*-hexane, is actually formed.

The boiling points of various mixtures of benzene and hexane have

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been determined by Jackson and Young (Trans., 1898, 73, 922), and a curve was drawn to represent the relation between the molecular composition and the boiling points. This curve is well reproduced by the formula $t = 68.97^\circ - 0.0134m + 0.001366m^2 - 0.041360m^3 + 0.061248m^4$, where t is the boiling point of the mixture and m the molecular percentage of benzene.

In the following table are given the molecular percentages of benzene and the boiling points, observed and calculated :

Molecular percentage of benzene.	Boiling points.			Molecular percentage of benzene.	Boiling points.		
	Observed	Calculated.	Δ		Observed	Calculated.	Δ
0	68.95°	68.97°	+0.02°	67.1	72.70°	72.64°	-0.06°
6.0	69.00	68.94	-0.06	69.4	73.01	72.97	-0.04
7.1	68.96	68.94	-0.02	79.6	74.67	74.71	+0.04
12.6	69.00	69.00	0	80.4	74.75	74.87	+0.12
18.6	69.14	69.12	-0.02	86.4	76.12	76.19	+0.07
29.8	69.47	69.50	+0.03	89.8	76.91	77.05	+0.14
33.8	69.72	69.72	0	90.9	77.20	77.35	+0.15
41.9	70.17	70.19	+0.02	92.7	77.75	77.85	+0.10
49.1	70.70	70.72	+0.02	94.5	78.49	78.38	-0.11
49.9	70.70	70.79	+0.09	95.7	78.80	78.74	-0.06
55.4	71.42	71.28	-0.14	100.0	80.20	80.17	-0.03

The formula appears to represent the results with sufficient accuracy to permit of its being employed for the calculation of the minimum boiling point. The calculated boiling points for mixtures containing 1, 2, . . . 10 per cent. are given below, and it will be seen that the minimum boiling point is 68.935°, or 0.035° below the calculated boiling point of *n*-hexane.

Molecular percentage of benzene.	Boiling point calculated.	Molecular percentage of benzene.	Boiling point calculated.
0	68.970°	6	68.936°
1	68.958	7	68.939
2	68.949	8	68.944
3	68.942	9	68.951
4	68.937	10	68.960
5	68.935		

It would appear from the above table that the mixture of minimum boiling point contains about 5 mols. per cent. of benzene, but the actual composition is somewhat uncertain owing to the flatness of the curve in this neighbourhood.

The estimation of the composition of a mixture by distillation is possible when the separation of the components, whether single substances or mixtures of constant boiling point, is practicable. In the case of ethyl alcohol and water, where the separation would be that of alcohol-water from water, we found that repeated fractional distillation with the most efficient still-head failed to give the pure mixture of constant boiling point. From a mixture of benzene and *n*-hexane it is impossible to separate either pure hexane or a mixture of constant composition. The following facts, bearing on this point, may be noticed about the benzene-hexane mixtures. (1) Benzene must be added until the mixture contains about 16 mols. per cent. before the boiling point rises 0.1° above that of hexane; (2) the boiling point of a mixture containing equal molecular proportions is 70.8° , or the rise of temperature is only 1.85° out of 11.25° , the difference between the boiling points of the pure components; (3) the mixture which has the boiling point 74.6° , midway between those of hexane and benzene, contains 79 molecules per cent. of benzene.

The ethyl alcohol-water curve, constructed from the data given by Noyes and Warfel (*J. Amer. Chem. Soc.*, 1901, 23, 463), is very similar in form to the *n*-hexane-benzene curve, but cannot be represented by so simple a formula. The following facts may be stated. (1) Water must be added until the mixture contains about 25 molecules per cent. before the boiling point rises 0.1° above that of pure alcohol; (2) the boiling point of a mixture containing equal molecular proportions is about 79.8° , or the rise of temperature is only 1.5° out of 21.7° , the difference between the boiling points of the pure components; (3) the mixture which has a boiling point 89.15° , midway between those of alcohol and water, contains about 93.5 mols. per cent. of water.

On distilling mixtures containing from 15 to 25 per cent. by weight of water through the 18-column dephlegmator and calculating the percentage of water in the mixture of constant boiling point in the usual way from the weight of distillate below the middle point, values from 7.6 to 8, instead of 4.43, per cent. were obtained, showing that too much water was carried down. Referring back to the calculation of the composition of the ternary ethyl alcohol-benzene-water mixture from the first distillation, if we take 7.8 as the percentage of water in the binary W.A. mixture, the calculated composition of the ternary mixture would become :

A	18.2
B	74.3
W	7.5
	<hr/>
	100.0

which agrees very well with that directly observed.

General Conclusions.

From the foregoing results, it will be seen that the distillation method, provided a very efficient still-head is used, may in the great majority of cases be safely employed for the determination of the composition of a mixture. But it must be borne in mind that from a mixture of two liquids it is almost always more difficult to separate the more volatile than the other component, and, therefore, if the original mixture contains a relatively very small amount of the more volatile component, a second distillation may be necessary, and a large quantity of the original mixture would be required in order to give a sufficient amount of distillate for a second operation. In such a case, the best plan is to continue the distillation the first time until the boiling point of the less volatile constituent is reached. No separation into fractions is necessary, but the whole of the distillate should be employed for the second operation, and the weight below the middle point then ascertained. A double correction for loss by evaporation must be introduced.

As regards the separation of three or more substances from a mixture, it may be pointed out that, as a general rule, the order as regards facility of separation is as follows: (1) the least volatile component, (2) the most volatile component, (3) the intermediate components.

It appears to be only when the curve representing the relation between boiling point and molecular composition is exceedingly flat at either end, as is the case for ethyl alcohol-water and for *n*-hexane-benzene when the more volatile component is in large excess, that the method is inapplicable.

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