VII.—*Note on Mixtures of Constant Boiling Point.*

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In the year 1879, Thorpe (*Trans.*, 35, 544) made the observation that when a mixture of equal volumes of carbon tetrachloride and methyl alcohol was distilled, 46·5 per cent. of the whole boiled constantly between 55·6° and 55·9°, that is, nearly 10° lower than the boiling point of the more volatile component.

From the vapour density of the mixture of constant boiling point, 41·82, Thorpe found its percentage composition to be :

Carbon tetrachloride.....	78·1
Methyl alcohol	21·9
	<hr/>
	100·0

As the composition of such a mixture can, as a rule, be ascertained by distilling one of different but known composition through an efficient still-head and weighing the distillate that comes over below the middle temperature (*Trans.*, 1902, 81, 752), it was suggested by Dr. Thorpe that I should determine the composition of this mixture of constant boiling point by the distillation method in order to compare the result with that calculated from the vapour density.

The carbon tetrachloride and the methyl alcohol used for the purpose were obtained from Kahlbaum, and in both cases a single distillation through an 18-column Young and Thomas dephlegmator was sufficient to give material of perfectly constant boiling point.

The boiling points observed by Thorpe and myself are given below :

	Thorpe.	Young.
Carbon tetrachloride	76·6°	76·75°
Methyl alcohol	65·2	64·7

It has been shown (*Trans.*, 1902, 81, 718) that methyl alcohol can best be obtained free from water by distillation through an efficient

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still-head, and the fact that Thorpe's specimen boiled 0.5° higher than mine may indicate that his alcohol was not completely dehydrated.

Two mixtures containing excess of carbon tetrachloride and one with excess of methyl alcohol were distilled through a 5-column "evaporator" still-head and an additional observation of the boiling point was made. The results obtained are as follows:

Boiling Points.

		Pressure, mm.	Temperature.	
			observed	corr. to 760 mm.
I.	CCl_4 in excess... ..	757.5	55.60°	55.70°
II.	" " "	760.0	55.70	55.70
III.	$\text{CH}_3\cdot\text{OH}$ "	756.4	55.58	55.72
IV.	" " "	757.9	55.61	55.69

Mean 55.70

This agrees very well with Thorpe's value, $55.6-55.9^{\circ}$.

Composition.

	Weights taken.		Middle point.	Weight below middle point.		Composition of mixture of constant boiling point.	
	CCl_4 .	$\text{CH}_3\cdot\text{OH}$.		Observed.	Corrected.	CCl_4 .	$\text{CH}_3\cdot\text{OH}$.
I.	118.45	23.37	66.2°	112.83	113.18	79.35	20.65
II.	110.50	22.11	"	106.74	107.09	79.35	20.65
III.	81.75	41.00	60.2	101.85	102.20	79.99	20.01

In the second distillation, the loss was estimated by weighing both the distillate and the residue. The difference between the sum of these weights and that of the mixture taken was 0.36 gram, and, as there was not more than a single drop of liquid left in the still-head after cooling, the loss by evaporation was taken to be 0.35 gram in this and also the other two distillations. It will be seen that the two results obtained by distilling mixtures containing excess of carbon tetrachloride agree perfectly together, but that the percentage of methyl alcohol calculated from the weight of distillate from the mixture containing excess of that substance is 0.64 lower. The percentage of methyl alcohol found by Thorpe is 1.25 higher than the highest value found by the distillation method.

In order to find which value is the most correct, the distillates from I and II were mixed together and redistilled, and the specific gravity

of the distillate, which came over at a perfectly constant temperature, was determined at $0^{\circ}/4^{\circ}$, and was found to be 1.35280. A mixture of about the right composition was then made up and its specific gravity at $0^{\circ}/4^{\circ}$ was determined:

Weights taken.	Percentage composition.	Sp. gr. at $0^{\circ}/4^{\circ}$.
CCl_4 26.6315	79.40	1.35236
$\text{CH}_2\cdot\text{OH}$... 6.9100	20.60	
	<hr/> 33.5415	<hr/> 100.00

If there were no change of volume on mixing the two liquids together, the specific gravity would be 1.34992; conversely, if the volume of the mixture obtained by distillation had been equal to the sum of the volumes of its constituents, its specific gravity would have been $\frac{1.35280 \times 1.34992}{1.35236} = 1.35037$, and the percentage composition of a mixture of this specific gravity would be:

Carbon tetrachloride.....	79.44
Methyl alcohol	20.56
	<hr/> 100.00

We have thus the following data for the composition of the mixture of constant boiling point:

Distillation Method.

	Thorpe.	From excess of $\text{CH}_3\cdot\text{OH}$.	From excess of CCl_4 .	From sp. gr. of distillate and made mixture.
CCl_4	78.1	79.99	79.35	79.44
$\text{CH}_3\cdot\text{OH}$	21.9	20.01	20.65	20.56
	<hr/> 100.0	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The last result, which agrees very well with that obtained by the distillation method when carbon tetrachloride was in excess in the original mixture, may probably be taken as the most correct.

The rather high percentage of methyl alcohol found by Thorpe may perhaps be partly accounted for by the presence of a trace of water, which would lower the vapour density of the mixture, but the chief cause of the error is, I believe, the difficulty of the separation of the mixture of constant boiling point from methyl alcohol, taken in conjunction with the fact that an ordinary distillation bulb was (presumably) used.

The following observations seem to confirm this view: When a pure liquid is distilled through a five-column "evaporator" still-head,

the drops which fall from the little funnels on the inverted tubes wet the glass at once and the liquid spreads itself in an even layer over the surface, unless the quantity of liquid in the flask is very small, when the vapour becomes considerably superheated and spheroidal drops may generally be seen in the lowest section, but not in the others. If, however, separation of the components of a mixture is taking place in the still-head, this is indicated by the formation of spheroidal drops.

In the distillation of mixtures of carbon tetrachloride and methyl alcohol, with the latter in excess, although the temperature of the vapour at the top of the still-head showed no rise until rather more than half the total quantity of liquid had come over, yet spheroidal drops were visible in the lowest section even at the beginning of the distillation, and they appeared in the second and third sections before the temperature showed any alteration. From this it appears that the vapour in the lowest section must have contained some excess of methyl alcohol during even the earliest stages of the distillation, and with an ordinary still-head this would be carried over and the percentage of methyl alcohol in the distillate would consequently be too high. It might, perhaps, be supposed that the temperature of the vapour would be appreciably raised by the presence of a small excess of methyl alcohol, but that this is not the case is proved by the fact that striæ, due to the great difference between the densities of methyl alcohol and of the mixtures of minimum boiling point, were clearly visible in the distillate as each drop fell, before the boiling point showed any sensible rise, and that they were very marked indeed when the temperature had risen 0.2° .

Thorpe states that the distillate, the vapour density of which was determined, boiled constantly between 55.6° and 55.9° , and I think that this small rise of 0.3° would be quite sufficient to account for the presence of a very appreciable excess of methyl alcohol, and if, as is almost certain, the separation was not quite perfect even at first, the 1.34 per cent. excess of alcohol is completely accounted for.

When mixtures containing excess of carbon tetrachloride were distilled through the 5-column "evaporator" still-head, no spheroidal drops were seen, even in the lowest section, until more than two-thirds of the total quantity had come over. It may therefore be concluded that the separation of the mixture of minimum boiling point from carbon tetrachloride is much easier than from methyl alcohol, and the following observations bear out this conclusion. (1) The spheroidal drops became very marked in the bottom section before they appeared at all in the second; (2) at a later stage, when the spheroidal drops had become very distinct in the third section, they had almost disappeared again in the lowest; (3) they had ceased to be visible in the

lowest section before the thermometer showed a marked rise, proving that at this stage the vapour in the tube above the top section consisted of the nearly pure mixture of constant boiling point, while that in the lowest section was nearly pure carbon tetrachloride; (4) the rise of temperature, when it at last took place, was exceedingly rapid, amounting, near the middle point, to about two degrees between two consecutive drops of distillate. It may be mentioned that in the distillations with carbon tetrachloride in excess, striæ were visible in the distillate before the thermometer indicated any perceptible rise of temperature. Of course the great difference between the density of the mixture of constant boiling point and that of either methyl alcohol or carbon tetrachloride makes the striæ in the distillate more easily visible than in the majority of cases, but the formation of these striæ in the distillate and, to an even greater extent, of the spheroidal drops in the still-head, generally affords useful indications of the progress of a distillation.

It is certain that if Thorpe's first distillate, coming over between 55.6 and 55.9° , had been redistilled, or if the original mixture had contained excess of carbon tetrachloride, the boiling point would have been almost perfectly constant for a considerable time, and the percentage of methyl alcohol in the distillate would have been lower.

It has been stated that a mixture containing 20.60 per cent. of methyl alcohol has the specific gravity 1.35236 at $0^{\circ}/4^{\circ}$, whereas if there were no change of volume on mixing the constituents, the specific gravity would be 1.34992 . The corresponding volumes of a gram are 0.73945 and 0.74078 , and there is therefore a contraction of 0.00133 c.c. or 0.18 per cent. On the other hand, on mixing together 27.5 grams of carbon tetrachloride and 7.15 grams of methyl alcohol, there was a fall in temperature of 0.95° , so that when the two liquids are mixed together in the proportion required to form the mixture of constant boiling point, there is slight contraction accompanied by a distinct fall of temperature. This mixture, in fact, resembles that of *n*-propyl alcohol and water in many respects, as will be seen from the table below :

Molecular composition of mixture	CCl ₄ and CH ₃ ·OH.		C ₃ H ₇ ·OH and H ₂ O.	
	CCl ₄	CH ₃ ·OH	C ₃ H ₇ ·OH	H ₂ O
	44.59	55.41	43.17	56.83
	100.00		100.00	
Difference of boiling point from that of more volatile component.....	- 9.00°		- 9.47°	
Percentage contraction on mixing in the right proportion	0.18		1.9	
Fall of temperature.....	0.95		about 1.2	
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Appendix.

In the papers by Miss Fortey and myself on the properties of mixtures of the lower alcohols with water, with benzene, and with benzene and water (Trans., 1902, 81, 717), reference should have been made to papers by E. F. Thayer (*J. Physical Chem.*, 1898, 2, 382) and G. Ryland (*Amer. Chem. J.*, 1899, 22, 384). Thayer determined the boiling point, and, by means of Pulfrich's refractometer, the composition of the mixture of minimum boiling point which ethyl alcohol forms with benzene. The materials employed were not quite pure; the benzene, after agitation with sulphuric acid, was distilled through a Hempel's still-head, and showed a rise of 0.5° during the complete distillation, but the first and last 25 per cent. were rejected. The alcohol (95 per cent.) was dried with lime and copper sulphate and showed a rise of 0.3° during distillation through the same still-head, the first and last portions being again rejected.

Ryland gives a list of mixtures of constant boiling point which had previously been observed, and records the formation of more than 40 additional ones. In the case of methyl alcohol and benzene, and of ethyl alcohol and benzene, he shows that the percentage of alcohol in the mixture of minimum boiling point diminishes considerably as the pressure is reduced. The composition of the mixtures of benzene with these alcohols was determined by adding water and measuring the volume of benzene set free. The materials employed by Ryland do not appear to have been quite pure, for he gives a range of 0.5° for the boiling points of each of the three liquids.

Carveth (*J. Physical Chem.*, 1902, 6, 248) has also determined the boiling point of the mixture of ethyl alcohol and benzene by passing the vapour of alcohol into benzene, and of benzene into alcohol, and observing in each case the lowest temperature reached. He made experiments with absolute alcohol and commercial benzene, and also with the purest materials available.

The results obtained by Thayer, Ryland, Carveth, and by Young and Fortey are given below:

Boiling Points reduced to 760 mm.

	Thayer.	Ryland.	Carveth.	Young and Fortey.
Ethyl alcohol	—	77.5—78.0°	—	78.30°
Benzene.....	79.5°	79.0—79.5	—	80.20
Ethyl alcohol and benzene	67.6	67—68	67.6°*	68.24
Methyl alcohol.....	—	64.5—65	—	64.70
Methyl alcohol and benzene	—	57.5—58	—	58.34

* With absolute alcohol and commercial benzene, 68.15° and 68.3° .

Percentage of Alcohol in Mixture of Constant Boiling Point.

	Thayer.	Ryland.	Carveth.	Young and Fortey.
Ethyl alcohol and benzene	33.5	31.4—32.3	—	31.76
Methyl alcohol and benzene	—	38.4—39.0	—	39.55

The boiling points observed by Thayer, Ryland, and Carveth are, in nearly every case, lower than those found by Miss Fortey and myself. We found that the boiling point of the mixture of ethyl alcohol and benzene was noticeably depressed by even traces of water, and it was only when the alcohol was completely dehydrated that the temperature 68.24° was observed.

Ryland states that methyl, ethyl, *isopropyl*, and *amyl* alcohols can be separated from toluene by distillation, but that *n*-propyl alcohol and *isobutyl* alcohol form with it mixtures of minimum boiling point. It has, however, been found by Miss Fortey and myself that ethyl alcohol and toluene do form such a mixture boiling at 76.7° , and that a ternary mixture of ethyl alcohol, toluene, and water is formed, with the boiling point 74.55° . As *isopropyl* alcohol resembles ethyl alcohol so closely in its properties, it seems almost certain that this alcohol would also form binary and ternary mixtures of constant boiling point with toluene and with toluene and water respectively.

Ryland also states that *isobutyl* alcohol and benzene can be separated by distillation, but this statement does not agree with our observation (*Trans.*, 1902, **81**, 748) that a mixture of minimum boiling point is formed. In this case, however, the boiling point, 79.93° , is very close to that of benzene, 80.2° , and the mixture contains only 9.3 per cent. of the alcohol. It is obviously impossible that very much time could have been devoted by Ryland to the purification of the large number of liquids he investigated, and as the mixtures were distilled only once with a plain still-head, it is not to be wondered at that the existence of the *isobutyl* alcohol-benzene mixture of constant boiling point should have escaped his notice.

To obtain trustworthy results, especially in the more difficult cases, it is necessary that the materials employed should be very carefully purified, and that an efficient still-head should be used.

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