LXVIII.—*Fractional Distillation with a Still-head of Uniform Temperature.*

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IN a paper on "The Comparative Value of Different Methods of Fractional Distillation" (this Journal, 1880, Trans., 49), I described an apparatus, by means of which the vapour evolved by a mixture of liquids in ebullition could be made to ascend a long tube, maintained at a constant temperature, before passing into the condenser of the distilling apparatus. If the temperature of this tube be less than that of the vapour which enters it from the still, partial or total condensation must take place, resulting in the former case in the return to the still of a mixture richer in the liquid of higher boiling point than the vapour, and consequently in the production of a distillate richer in the liquid of lower boiling point than the same vapour. The process of fractional distillation is therefore improved by the introduction of a still-head of constant temperature, as was shown long ago by Warren (*Memoirs of the Amer. Acad.*, New Series, 9), a picture of whose apparatus is given in the fifth edition of *Miller's Chemistry*, 3, Section I, p. 8. Warren's apparatus, though well adapted to all ordinary requirements, is ill-suited to exact scientific experiments, on account of the difficulty of maintaining a constant temperature in the still-head. This difficulty is chiefly due to the continual but irregular heating of the liquid surrounding the still-head by the vapour from the still, this source of heat being often so considerable as to necessitate the use of a current of water to keep down the temperature.

In the apparatus referred to above, and shown on the left hand of the figure accompanying this paper, the heat brought to the still-head by the vapour from the still merely increases the rate of ebullition of the liquid surrounding the coiled tube, and does not raise the temperature, the reading of the thermometer in the still-head being in fact entirely independent of the distillation. Hence it is possible to conduct a long distillation without fear of any variation in the temperature of the still-head, and if necessary, to repeat it, or to make a second with a different mixture at the same temperature.

Although it is generally recognised that the use of Warren's apparatus is very advantageous, the laws which govern the process have hitherto been unknown; it seemed to me therefore to be desirable to submit the whole matter to investigation, more especially as the work promised to yield results of considerable theoretical import-

ance. Thus, in the paper above referred to, four distillations of mixtures of benzene and carbon disulphide were given, in which the temperatures of the still-head were 57.1° , 70.1° , 46.5° , and 46.5° respectively. These distillations resulted in each case in a distillate of uniform composition, while in the last two the distillate consisted of almost pure carbon disulphide, a result which seemed incompatible with the fact that at 46.5° the tension of the vapour of benzene is nearly 240 mm. Postponing till the close of this communication any attempt to explain this and similar anomalies, I proceed at once to describe the experiments which I have made upon the subject.

The complete apparatus employed is shown in the figure. A is the still, *cc* the copper coil serving as still-head; E the cylinder surrounding it, and containing some liquid kept in ebullition by the burner *b*; HH the condenser, R the receiver, while the portion to the right of R represents the apparatus for maintaining any constant pressure in the cylinder E, and consequently any constant temperature; this last-mentioned apparatus I have recently described in a paper on "The Distillation of Mixtures of Carbon Disulphide and Carbon Tetrachloride" (this Journal, 1881, Trans., 304); it communicates with the cylinder E by means of the tube *qqq*. A thermometer, T_1 , was placed in the tube *aa*, and a second thermometer, T_2 , in the upper end of the coil *cc*. For a more complete description the reader is referred to the papers mentioned above.

The thermometer T_2 was always one which had been compared with the standards used in all these researches, and a correction was made for any difference of reading observed; the index error of the thermometer was also allowed for. The thermometer T_1 being merely employed to show the general absence of variation in the temperature of E, its readings were not corrected. In any case these corrections are not of much value, as the distillations were carried out under the ordinary barometric pressure, and from the nature of the case no reduction could be made to the standard pressure of 760 mm. The general nature of the result is, as will be seen, unaffected by any small errors arising from this cause.

The first experiments were made with mixtures of carbon disulphide and carbon tetrachloride, the composition of which was determined by observing the density, as in previous cases. The liquids were purified with great care, as described before (*loc. cit.*, p. 306).

The burner *b* having been lighted, and the apparatus for constant pressure suitably adjusted, the ebullition of the liquid in E (in this case methylated spirit) was allowed to proceed for a short time until the reading of the thermometer T_1 remained constant. The still A, consisting of a glass flask, and containing about a pint of a mixture of the two liquids, was then adapted to the lower end of *cc*, and gradu-

ally heated, when the mixture began to boil. It sometimes happened that the temperature of its vapour was below that of the still-head; in this case it is evident that the vapour ascended the coil unchanged, and passed into the condenser just as if no still-head were present; but as the mixture in the still became richer in CCl_4 , the temperature of the vapour evolved necessarily rose, until it exceeded that of the still-head; partial condensation then took place, indicated by a continual dropping from the lower end of C. Only when this return of liquid to the still became well marked were the fractions tabulated below collected.

As the experiment proceeds, the proportion of CCl_4 in the still increases, the condensation in the still-head becomes relatively greater, and the distillation slower and slower, until at length the whole of the vapour generated in the still condenses in the still-head, and the distillation ceases. The process is therefore limited at both ends, commencing when the boiling point of the mixture in the still equals the temperature of the still-head, and ending when the mixture in the still has reached a certain composition, of which more anon. The fractions, of which the densities and percentage composition (reckoned as in previous papers in molecules) are given in the following table, generally constituted together nearly the whole of the possible distillate, and amounted to a considerable fraction of the whole mixture employed. In each case therefore the mixture in the still varied very greatly in composition during the experiment. In some of the distillations the percentage was determined at the commencement and at the end of the process; where this was done, the results are given in the first column. The thermometers were read at equal intervals of time throughout the experiment, the mean reading for each fraction being given. In other respects the following table of ten distillations requires no explanation:—

General remarks.	Number of fraction.	Reading of therm. T_1 .	Reading of therm. T_2 (corrected).	Density of fraction corrected to 20°.	Percentage of CCl_4 in fraction.
A	I....	48·65	48·45	1·29894	6·89
	II....	48·65	48·45	1·29803	6·69
	III....	48·65	48·40	1·29732	6·54
	Mean ..	48·65	48·43	1·29810	6·71
B	I....	52·00	51·80	1·33820	15·68
	II....	52·00	51·90	1·33835	15·72
	III....	52·00	51·80	1·33788	15·60
	Mean ..	52·00	51·82	1·33814	15·67
C	I....	59·37	59·29	1·41425	35·20
	II....	59·37	59·25	1·41379	35·08
	Mean ..	59·37	59·27	1·41402	35·14
D	I....	63·65	63·58	1·45925	48·55
	II....	63·69	63·59	1·45893	48·45
	Mean ..	63·67	63·59	1·45909	48·50
E	I....	66·34	66·35	1·48740	57·64
F	I....	71·87	71·73	1·54502	78·39
	II....	71·84	71·80	1·54487	78·33
	III....	71·82	71·73	1·54607	78·79
	Mean ..	71·84	71·75	1·54532	78·50
H carried to limit....	I....	69·10	68·91	1·51783	68·24
K carried to limit....	I....	69·14	69·00	1·52156	69·59
L carried to limit	I....	56·00	55·80	1·38092	26·32
	II....	56·01	55·82	1·38134	26·21
	Mean ..	56·00	55·81	1·38113	26·27
M carried to limit....	I....	56·18	55·96	1·38653	27·68
	II....	56·13	55·80	1·38549	27·41
	Mean ..	56·15	55·88	1·38601	27·54

An inspection of the above table leads to the conviction that the composition of the vapour issuing from the top of the coil is dependent on the temperature of the coil, and upon that only, remaining constant while the composition of the boiling liquid changes. This result is identical with that foreshadowed by the experiments detailed at the close of my paper referred to above (this Journal, 1880, 58).

We have now to inquire what relation exists between the temperature of the coil and the composition of the distillate.

Referring to the curves expressing the distillation of CS_2 and CCl_4 , or to Tables XXVIII and XXIX (this Journal, 1881, 310), we can easily obtain the temperature at which a vapour of particular com-

position is evolved by a mixture of the two substances boiling under the ordinary pressure, or in other words, find the boiling point of that mixture which evolves a vapour of given composition.

In the following table the first column gives the mean composition of the vapour issuing from the still-head in each of the above distillations; the second column gives the temperature of the still-head; the third column the composition of the mixture, which on ebullition evolves vapour, having the composition mentioned in the first; while the fourth column contains the boiling point of such mixture.

Percentage of CCl_4 in vapour as observed.	Temperature of still-head.	Percentage of CCl_4 in mixture evolving vapour given in column I.	Boiling point of mixture mentioned in column III.
6·7	48·4	14·1	48·1
15·7	51·8	32·9	51·5
35·1	59·3	61·3	59·4
48·5	63·6	73·2	63·7
57·6	66·4	80·0	66·5
78·5	71·8	91·6	72·1
68·2	68·9	86·7	69·6
69·6	69·0	87·4	70·0
26·3	55·8	50·7	56·0
27·6	55·9	52·2	56·5

On comparing the numbers in the second and fourth columns, and remembering that no correction has been made for varying barometric pressure, it will be recognised that in the first six cases they are practically identical; in the remaining four cases the agreement is not so good, but this arises from the conditions under which these experiments were made, viz., with a large percentage of CCl_4 in the still and an extremely slow distillation. Under such circumstances it would be expected that the percentage of CCl_4 in the distillate would be somewhat greater than under more usual conditions, and consequently the boiling point of the corresponding mixture higher. We are therefore led to the following general statement:—*In distillations with a still-head maintained at a constant temperature, the composition of the distillate is constant, and is identical with that of the vapour evolved by a mixture whose boiling point equals the temperature of the still-head.* We shall see that this statement is fully confirmed by other experiments made with other liquids.

Before passing to those confirmatory experiments, I should like to draw attention to one or two matters of great practical, though of little theoretical, importance. It has been already mentioned that as the mixture in the still becomes richer in CCl_4 , the proportion of the

evolved vapour which is returned to the still rapidly increases, while the remainder which finds its way to the receiver as rapidly diminishes; there is therefore a limit to the proportion of CCl_4 in the still, beyond which distillation becomes impossible.

With a view to ascertain whether this limit was susceptible of any general definition applicable, like the statement given above, to all mixtures of a normal character, the last four distillations, H, K, L, and M, were continued until the delivery of liquid from the end of the condenser dwindled to an occasional drop. The percentage of CCl_4 in the residue in the still was then determined, and was found to be as follows:—

H	99.2
K	99.4
L	93.2
M	91.9

Bearing in mind the fact that with mixtures of carbon disulphide and benzene a mixture containing 38 per cent. of CS_2 was obtained as distillate, when the mixture in the still contained only 4.3 per cent. of CS_2 , or 95.7 per cent. of benzene, we are led to the conclusion that the absolute or theoretical limit is reached only when the still no longer contains any of the liquid of lower boiling point, but that this limit becomes more and more difficult to attain, as the temperature of the still-head is reduced. A further prosecution of the enquiry in this direction seemed therefore of little value, more especially as the experiments coincided with the conclusions derived from the explanation of the whole matter, which will be given further on.

A second point of interest was the composition of the mixture returned to the still by condensation in the still-head. With a view to determine this, two distillations were made with a test-tube, suspended below the lower end of the tube *cc*, so as to catch the liquid dropping back; the distillation was interrupted, and the test-tube removed when it was full. During the first distillation the still-head was maintained at 56.8° , and two successive samples of the returning liquid were collected; the first contained 60.4 per cent. of CCl_4 , and the second 69.2 per cent. During the second distillation the still-head was kept at 57.1° , and four fractions of the returning liquid were collected; they contained respectively 60.9, 64.8, 68.9, and 74.1 per cent. of CCl_4 . Remarking that the first drop which is returned to the still when the vapour which enters the still-head has a temperature equal to or slightly exceeding that of the coil, must have the same composition as the boiling mixture, and that at the limit the returning liquid must be pure CCl_4 , we see that the percentage of CCl_4 gradually

increases throughout the distillation, but that it cannot be defined more exactly.

I now pass to a series of experiments with mixtures of carbon disulphide and benzene, which were conducted in a manner precisely similar to those given in the first table in this communication. In the following table the experiments given at the close of the paper on the comparative value of different methods of fractional distillation (*loc. cit.*) are included. The percentages given being those of CS₂, the most volatile liquid, instead of the least volatile, as in the previous case, the table has a slightly different aspect:—

General remarks.	Number of fraction.	Reading of therm. T ₁ in cylinder.	Reading of therm. T ₂ (corrected).	Density of fractions at 19·80.	Percentage of CS ₂ in fraction.
A	I....	70·29	69·94	0·98826	38·44
	II....	70·35	69·98	0·98516	37·48
	III....	70·57	70·23	0·98498	37·42
	IV....	70·56	70·24	0·98527	37·52
	Mean ..	70·44	70·10	0·98592	37·71
B. Residue contained 2·4 p. c. of CS ₂ .	I....	63·81	63·76	1·05305	56·66
	II....	63·73	63·47	1·05606	57·43
	Mean ..	63·77	63·61	1·05456	57·04
C	I....	57·50	57·10	1·13523	75·73
	II....	57·50	57·10	1·13185	75·02
	III....	57·50	57·10	1·13348	75·36
	IV....	57·50	57·10	1·13528	75·74
	V....	57·52	57·12	1·13649	75·99
	VI....	57·51	57·10	1·13656	76·01
	VII....	57·53	57·12	1·13733	76·17
	VIII....	57·53	57·30	1·13819	76·35
	IX....	57·53	58·00	1·13358	75·38
	X....	57·53	57·90	1·13333	75·33
	Mean ..	57·52	57·29	1·13513	75·71
D	I....	52·74	52·55	1·18001	84·80
	II....	52·74	52·55	1·18008	84·81
	III....	52·74	52·50	1·18058	84·90
	IV....	52·74	52·40	1·18132	85·05
	Mean ..	52·74	52·50	1·18050	84·89
E. Residue contained 17·8 p. c. of CS ₂ .	I....	49·00	48·92	1·22743	93·43
	II....	49·00	48·83	1·22529	93·05
	III....	49·00	48·85	1·22789	93·51
	Mean ..	49·00	48·87	1·22687	93·33

The above five distillations confirm the statement previously made, that the composition of the vapour issuing from the coil is dependent only upon the temperature of the coil.

The following table corresponds exactly with that given for CS_2 and CCl_4 , on page 520, the numbers in the third and fourth columns being obtained from the curves referred to in a paper on "The Theory of Fractional Distillation" (this Journal, 1879, Trans., 547).

Percentage of CS_2 in issuing vapour as observed.	Temperature of issuing vapour.	Percentage of CS_2 in mixture evolving vapour given in first column.	Boiling point of mixture given in third column.
37·7	70·1°	13·3	70·2°
57·0	63·6	26·3	63·6
75·7	57·3	46·9	56·7
84·9	52·5	64·0	52·1
93·3	48·9	83·7	48·6

Comparing the numbers given in the second and fourth columns, we see that they agree fairly well together, thus confirming the general statement made on page 521.

The experiments which yielded the data necessary for determining the above-mentioned curves were made with imperfect apparatus; had the apparatus been of the improved form used in the experiments on mixtures of CS_2 and CCl_4 , it is probable that the numbers in the two columns would have been still more nearly equal.

A series of distillations were now made with mixtures of alcohol and water, with a view of ascertaining whether the laws governing the above experiments were also applicable in this case, in which the two substances mixed exert a certain action one upon the other. The cylinder surrounding the coil was filled with water, the boiling point of which was regulated by reducing the pressure as before. The composition of the various fractions, &c., was determined by observing their densities at 20°. The numbers in the following tables give the percentage of alcohol *by weight* and *not in molecules*, as in the previous cases. The densities at 20° of mixtures of alcohol and water have been determined by many persons, and among them by Mendeleeff (*Pogg. Ann.*, **138**, 103 and 230; *Watts's Dict.*, 2nd Supp., 476), whose numbers I have employed to obtain the percentages corresponding to the densities observed.

The table of densities given by Mendeleeff is based on experiments in which the weighings were reduced to a vacuum; it becomes therefore a question of some importance whether this correction must be made in the experiments given below:—

If W_1 = apparent weight of tube + mixture,
 „ W_2 = „ „ „ + water,
 „ W_3 = „ „ „ empty,

we have $D_1 = \text{apparent density} = \frac{W_1 - W_3}{W_2 - W_3}$. If $D = \text{the true density}$, $e = \text{weight of 1 c.c. of air} = .0012 \text{ gram}$, $N = \text{the density of the weights}$, $V = \text{volume of air displaced by the empty tube}$, we have evidently—

$$D = \frac{W_1 + e \left(\frac{W_1 - W_3}{D} + M - \frac{W_1}{N} \right) - W_3 - e \left(M - \frac{W_3}{N} \right)}{W_2 + e \left(\frac{W_2 - W_3}{1} + M - \frac{W_2}{N} \right) - W_3 - e \left(M - \frac{W_3}{N} \right)},$$

$$\text{or } D = \frac{W_1 - W_3 + e \frac{W_1 - W_3}{D} - e \frac{W_1 - W_3}{N}}{W_2 - W_3 + e (W_2 - W_3) - e \frac{W_2 - W_3}{N}},$$

$$\text{or } D = \frac{W_1 - W_3}{W_2 - W_3} \left\{ \frac{1 + \frac{e}{D} - \frac{e}{N}}{1 + e - \frac{e}{N}} \right\}$$

$$\text{or } D = D_1 \frac{1 + \frac{e}{D} - \frac{e}{N}}{1 + e - \frac{e}{N}}.$$

If in this expression we make $N = 8$, and $D = D_1$, we obtain the following corrections to the densities, as observed by weighing in air:—

Densities.	Corrections.
0.79	+ 0.00025
0.85	+ 0.00018
0.90	+ 0.00012
0.95	+ 0.00006
1.00	+ 0.00000

In the following tables corrections are made corresponding with the above, though the error incurred by neglecting them would have been scarcely appreciable.

The densities are referred to water at 4° , and not at 20° . In other respects the distillations correspond exactly to those made with mixtures of CS_2 with CCl_4 and C_6H_6 respectively.

	No. of fraction.	Reading of T_1 in cylinder.	Reading of T_2 in top of coil (corrected).	Density reduced to 20° and corrected for weighing in air.	Percentage of alcohol in fraction.
A	I	77·67	78·40	0·82052	89·05
	II	"	"	0·82026	89·15
	III	"	"	0·82006	89·22
	IV	"	"	0·81963	89·38
	V	"	"	0·81926	89·56
	Mean ..	"	"	0·81995	89·27
B	I	81·97	81·64	0·85142	76·80
	II	82·02	81·78	0·85218	76·49
	III	82·23	81·99	0·85318	76·08
	Mean ..	82·07	81·80	0·85226	76·46
C	I	86·77	86·53	0·87762	65·84
	II	86·82	86·54	0·87752	65·88
	Mean ..	86·80	86·54	0·87757	65·86

The numbers in the last column of this table show that in this case also the composition of the distillate does not vary when the temperature of the coil remains constant; it will be noticed that in the first experiment A, the proportion of alcohol slightly increased as the distillation progressed; this is due to the more effectual action of the coil upon the ascending vapour as the rate of distillation diminishes. In the second experiment, B, the temperature rose slightly, and consequently the percentage of alcohol diminished from fraction to fraction; the general constancy of the distillate is, however, evident.

It remains for us to learn whether the vapour containing 76·46 per cent. of alcohol issuing from the coil when the temperature is $81·80^\circ$, is identical in composition with that which is emitted by a mixture boiling at $81·80^\circ$, and the same in the case of the third experiment.

The composition of the vapours given off by spirit of different strengths, together with the boiling points of such mixtures, have been determined by Gröning and many other observers; the discrepancies of the different tables to be found in works on alcoholometry are, however, so great that I thought it simpler to make the necessary experiments myself. With this object the copper still furnished with a jacket, and described by me in a previous paper (this Journal, 1881, Trans., 311), was filled with a mixture of alcohol and water boiling a little below the requisite temperature, and the distillation allowed to proceed until the thermometer rose to that temperature; a sufficient quantity of the distillate was then collected separately, while the thermometer reading remained constant, and its density and composition determined in the usual manner. The same thermometer, T_2 , was used,

and the experiments were made on a day when the barometer stood at very nearly the same height as when the experiments recorded in the above table were made. Two distillations were made and fractions collected each time at 81.80° ; the density of the distillate passing over at this temperature was found to be, in the first experiment, 0.85263; and in the second, 0.85254; the mean, 0.85258, corresponds with 76.32 per cent. of alcohol, which agrees well with the number 76.46, obtained in the coil. Two distillations were also made in which fractions were collected at 86.50° ; their densities were found to be 0.87752 and 0.87756 respectively; the mean, 0.87754, corresponds with 65.88 per cent. of alcohol, which is exactly the quantity of alcohol contained in the distillate from the coil at the same temperature. There can therefore be no doubt that the distillate from the still-head is always identical with that from a mixture boiling at the temperature of the still-head.

A mixture of two liquids containing an indefinitely small quantity of the liquid of higher boiling point boils at a temperature but little removed from the boiling point of the more volatile substance, and emits a vapour which contains this substance only; if therefore we keep the still-head at that temperature, we ought by the law above stated to obtain a distillate consisting wholly of the more volatile substance whatever may be the composition of the mixture in the still, and thus effect a complete separation of the two liquids at one operation. In order to see whether this deduction from the law could be verified in practice, a number of distillations were made with different mixtures, the still-head being always maintained at the lowest possible temperature, which was (except in special cases) the boiling point of the more volatile substance.

Carbon Disulphide and Benzene.—In a paper previously referred to (this Journal, 1880, Trans., 59), experiments were recorded in which it was proved that a distillate containing 98 per cent. of CS_2 could be obtained even from a mixture containing only 25 per cent. of that substance.

Benzene and its Homologues.—In the same paper it was shown that practically pure benzene could be obtained from very crude material by maintaining the coil at 80.5° .

Carbon Disulphide and Carbon Tetrachloride.—Two experiments were made with mixtures of these two substances, the temperature of the still-head being as low as was compatible with a tolerably rapid distillation; when a mixture containing 63 per cent. of CS_2 was put in the still and the still-head maintained at 47.1° , the distillate was found to contain 97.3 per cent. of CS_2 ; with a mixture

containing 55 per cent. of CS_2 , and the still-head at 47.5° , a distillate containing 95.9 per cent. of CS_2 passed over. These numbers are not the best attainable, since the temperature of the still-head in both cases considerably exceeded that at which CS_2 boils, viz., 46.5° ; if, however, the temperature be allowed to approach this limit more nearly, the distillation becomes very slow, and finally almost impracticable. It should also be remembered that the above percentages are reckoned in molecules, and that the percentages of CS_2 by weight would be about 98.6 and 98.0 respectively.

Carbon Tetrachloride and Toluene.—Two distillations were made with mixtures of these substances; in the first the liquid in the still contained 70.2 per cent. of CCl_4 , while the distillate obtained when the still-head was kept at 76.6° contained 98.83 per cent. of CCl_4 . In the second experiment the liquid in the still contained 51.4 per cent. of CCl_4 ; practically no distillation took place until the temperature of the still-head was raised to 79° ; between this temperature and 80° , a considerable quantity of distillate was collected, the density of which showed that it contained 96 per cent. of CCl_4 ; the percentages in this and in the following cases express the relative weights of the two substances, and not the relative numbers of molecules.

Benzene and Dibromethane.—In this case also two distillations were made, the first with a liquid containing 55.7 per cent. of benzene, the second with one containing 65.1 per cent. The still-head being at 80° , a considerable proportion of the liquid distilled over in each case; the densities of the distillates collected were determined, and showed that they contained 99.7 and 99.8 per cent. of benzene respectively.

The above experiments show that it is possible to obtain a liquid almost entirely free from another with which it has been mixed, by means of a still-head kept at a sufficiently low temperature; the deduction from the general law is therefore verified.

Practically the process is limited in its application, on account of the great condensation in the still-head which takes place when the mixture in the still contains a large percentage of the liquid of higher boiling point; the waste of time and fuel then becomes disproportionate to the result obtained.

All the liquid mixtures hitherto considered with regard to this question of complete separation belong to one class, each consisting of substances which mix in all proportions, and between which no combination of any kind is known to take place; among this class of mixtures there are, however, some which behave in an abnormal manner, their condition approximating apparently to that of two liquids which are in contact but do not mix. In this latter case, as is

well known, the boiling point of the mixture is much lower than that of either of the two substances (see this Journal, 1879, Trans., 547); in the same way the boiling points of many mixtures, in which one of the two liquids is an alcohol or other substance containing hydroxyl, methoxyl, or some other derivative of hydroxyl, and the other a hydrocarbon, a chlorinated hydrocarbon, or generally a substance which does not contain hydroxyl, are often lower than that of either of the constituent substances. When this is the case, it is evident that if the still-head is maintained at the boiling point of the most volatile substance, that substance will not pass over alone; on the contrary, the distillate will have the composition of the vapour evolved by that mixture, which boils at the temperature of the still-head. That such a mixture must exist is clear, when we remember that the boiling point varies continuously when the composition of the mixture varies, and that some mixtures have a lower boiling point than that of the most volatile substance.

As examples of such mixtures, we may take those of carbon disulphide and alcohol, and carbon disulphide and acetic ether.

Carbon Disulphide and Alcohol.—Pure ethyl alcohol was digested twice with quicklime, and was finally distilled from a fresh quantity of that substance; its density at 20° referred to water at 20° was then found to be 0.79322. According to Mendeleeff (*Pogg. Ann.*, **138**, 103 and 230) the density of absolute alcohol at 20° referred to water at 4° is 0.78945; referred to water at 20° this would be 0.79079, whence the above alcohol contains 0.8 per cent. of water. The number 0.79079 is taken as the true density of alcohol, while 1.26575 was that of the carbon disulphide employed. As the change of volume resulting from the mixture of alcohol and CS₂ is unknown, we must content ourselves with supposing that no such change takes place: in this case if—

- x = percentage of weight of CS₂ in any mixture,
- D = density of that mixture,
- D_1 = density of CS₂,
- D_2 = density of alcohol,

the value of x is given by the equation—

$$x = \frac{100 D_1 (D - D_2)}{D (D_1 - D_2)}.$$

The cylinder surrounding the still-head having been filled with carbon disulphide boiling at the ordinary pressure, two distillations, A and B, were made.

A. The mixture in the still at the commencement of this distillation

contained 36.6 per cent. of CS_2 , and at the end 2.6 per cent.; the distillate was collected in three portions, which contained respectively 87.1, 87.4, and 87.2 per cent. of CS_2 .

B. In this second distillation the composition of the liquid in the still was not determined; a large fraction of the distillate which was collected contained 87.4 per cent. of CS_2 .

Carbon Disulphide and Ethyl Acetate.—The ethyl acetate employed was purified by fractional distillation and dried, but it was not very pure; its density at 20° was 0.88607.

The still-head being surrounded as before with boiling CS_2 , two fractions were collected which contained respectively 72.7 and 72.4 per cent. of CS_2 .

These examples suffice to show the difference between the results obtained with such mixtures and those derived from the distillation of the normal mixtures, such difference arising, as was before remarked, from the fact that their vapour-tensions are higher than those of either of the constituent substances. This singular variety in mixtures which have the same outward appearance will, I hope, form the subject of a future communication.

Alcohol and Water.—When a mixture of alcohol and water is boiled in the still, and the temperature of the still-head is very gradually raised, no distillation takes place until the thermometer reaches 78° ; if the still-head be then kept at this temperature, the distillate is found to be uniform in composition, and to contain 90.7 per cent. of alcohol; it is therefore impossible to obtain absolute alcohol by this process, the reason apparently being, as we shall see presently, that a spirit containing 90.7 per cent. of alcohol evolves when boiled a vapour of the same composition as itself.

We have now to endeavour to explain the various facts described above, and to understand how it is, that when a mixture of two substances is distilled, the vapour issuing from the still-head is constant in composition and contains as much of each of the two substances as does the vapour which is evolved by that mixture which boils at the temperature of the still-head. At first sight it would appear almost incredible that when a mixture of two vapours is made to pass through a tube which is just hot enough to prevent the condensation of one of them, that one and that only should issue from the other end. If a current of air be made to pass through a tube, the sides of which are wetted with benzene or any other volatile liquid, it will, as is well known, carry with it a quantity of that substance dependent on the vapour-tension of the liquid, and consequently on the temperature of the tube: why then does a current of carbon disulphide gas escape

from such a tube almost completely free from benzene? The answer to this question must, I think, be sought in the different action of the molecules of benzene upon those of air and of carbon disulphide respectively. That such a difference does exist is made manifest by the fact that mixtures of CS_2 and C_6H_6 can be made having any required boiling point between 46.5° and 80.2° , whereas it is known that no mixture of air and benzene can be obtained having a boiling point between 0° and 80° , while there is no probability that any mixtures having lower boiling points can exist. Now the absence of a series of mixtures having boiling points varying continuously from that of the more volatile to that of the less volatile substance is characteristic of two liquids which do not mix, for a mass containing two such liquids has the same boiling point whatever may be the proportion in which they are present. We may therefore presume that air and benzene, or more strictly speaking, nitrogen or oxygen and benzene, are substances which do not mix in the liquid state, and we may ascribe to this fact the different result obtained when their mixed vapours are passed through a tube.

When a mixture of two liquids which mingle in all proportions is heated to ebullition, it evolves, as we have repeatedly seen before, a mixed vapour containing a certain proportion of each of the two substances, the liquid mixture and the gaseous mixture being mutually related and existing together in a state of equilibrium. If an infinitesimally small quantity of heat be added to the mass, it will result in the formation of more of the gaseous mixture, if on the other hand, a similar quantity of heat be abstracted, the slight condensation taking place will yield an additional quantity of the liquid mixture. It is, I think, on this reciprocity between the liquid and the vapour, that depends the action of the still-head in fractional distillation.

In order to render this clear, let us imagine a mixture of two liquids, A and B, to be placed in the still, the boiling point of such mixture being θ , while the boiling point of A is t_1 , that of B, t_2 : let T be the temperature of the still-head, and let $t_1 < T < \theta < t_2$. As the mixed vapour evolved by the liquid in the still ascends the tube forming the still-head, its temperature will gradually sink from θ to T. Let us divide this period of cooling into n very small intervals; during the first of these the condensation of the vapour will result in the formation of a small quantity of liquid having the composition of the mixture in the still. Since the liquid mixture is in all ordinary cases poorer in A than the corresponding gaseous mixture, this condensation will leave the rest of the vapour richer in A. During the second period of cooling, this remaining gaseous mixture will be partially condensed, yielding a very small quantity of the liquid mixture to which it is related. This second period will therefore again

add to the proportion of A in the ascending vapour; the succeeding periods will do the same, and so on, until the gaseous mixture becomes identical with that evolved by a liquid mixture of which the boiling point is T, or in other words till the vapour becomes sufficiently rich in A to avoid further condensation; it then ascends the rest of the still-head unaltered, and passes into the condenser, its composition necessarily obeying the law indicated by the experiments detailed above. When $t_1 = T$, it is clear that the process of condensation and consequent enrichment in A will go on until that substance is left alone, for any gaseous mixture containing ever so little of the vapour of B will suffer partial condensation in a tube maintained at t_1 .

In the case of alcohol and water, a spirit containing about 90 per cent. of alcohol distils unchanged, the vapour and the corresponding liquid having the same composition. When therefore the ascending vapour reaches this strength, any further cooling produces total condensation; the process of enrichment can go no further, and if distillation takes place at all, the distillate can contain no more than 90 per cent. of alcohol.

The cases of alcohol and carbon disulphide and of ethyl acetate and carbon disulphide, are also fully met by the above explanation.

It appears to me that this *reciprocity* between a liquid mixture and the gaseous mixture which it evolves on ebullition, has been often neglected by those who have reasoned on these and similar questions, and that the arguments which they have brought forward have often been much reduced in value by such neglect.