V.—*The Comparative Value of Different Methods of Fractional Distillation.*

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WHERE fractional distillation is carried out on a large scale, various forms of apparatus of a somewhat complicated character are generally employed; though differing much in detail they are all designed to subject the mixed vapours to one or both of two well defined processes, which for the purposes of this paper may be termed respectively *washing* and *cooling*.

In the process of *washing*, the mixed vapours issuing from the still are made to pass through several layers of liquid obtained by their own partial condensation, they are thus *washed* by these successive layers, and it is supposed that the vapour of the liquid of highest boiling point is partially removed by this process, which results therefore in a distillate containing more of the liquid of lower boiling point than would be obtained by simple distillation.

There is at first sight, however, no reason to suppose that a mixture of vapours should be materially altered in composition by a liquid having about the same composition and the same temperature as itself. It would appear that the first step in the construction of these forms of apparatus resulted from an attempt to utilise the latent heat of the vapour given off by a weak spirit to distil a stronger one; the latent heat of the vapour of this second spirit might then be used to distil a third, and so on, thus effecting a series of distillations in the same apparatus with the same fuel. If this series of distillations actually took place, that is to say, if the vapours rising from the still really

condensed in the first layer of liquid, thus causing that liquid to boil and emit vapour, which condensed in the second layer, causing that to boil in its turn, the advantages of the process would be undeniable; but since apparently the vapours only pass through the layers of liquid, and may therefore remain nearly unaltered, the real value of this method of distillation can only be determined experimentally.

In the process of *cooling*, the mixed vapours are partially condensed, either by allowing radiation to take place, or by passing them through a coil kept at a given temperature; the liquid of highest boiling point suffers, of course, the most condensation, and runs back into the still, a better distillate being thus obtained. Now a possible explanation of the success of the first process is that the successive layers of liquid, by obstructing the passage of the vapour, give it more time to cool by radiation, and that thus the two processes are really one and the same.

With a view to learning whether these two processes of *washing* and *cooling* really differ in their effects, I have made the experiments now to be described.

Two distillations were first made, one with a form of apparatus advocated by Linneman (*Annalen*, **160**, 195), Le Bel and Henninger (*Compt. rend.*, **79**, 480), and others, designed to wash the vapours, and termed a dephlegmator, the other merely with a long ascending tube, suitable for partially condensing them. The liquids employed were carbon disulphide and benzene, selected for reasons given in a former paper (this Journal, 1879, 547). The composition of the several fractions of the distillates was determined by observing their densities in the manner described in the same paper. All the percentages given below represent the number of molecules of CS_2 in a hundred molecules of the mixture, assuming, of course, that the weights of the molecules of CS_2 and C_6H_6 are to one another as 76 is to 78.

Distillation with Dephlegmator.—547.5 grams of a mixture having a density of 1.07672 at 19.80° , and containing therefore 62.54 per cent. of CS_2 , were distilled from a flask, having a capacity of about a litre, and fitted with a dephlegmator having the form and dimensions shown in Fig. 1; the distillate was collected in the receiver described in the before-mentioned paper (this receiver was used also in all the subsequent distillations). The barometric pressure during the distillation was 773.7 mm. (corrected and reduced to 0°). The following table gives the details of the distillation:—

Number of fraction.	Temperature of distillation.	Weight of fraction.	Density at 19·80°.	Percentage of CS ₂ .
I.....	51·5—52·5	52·34	1·19562	87·71
II.....	52·5—54·0	105·41	1·17857	84·51
III.....	54·0—55·0	63·18	1·16230	81·29
IV.....	55·0—56·5	81·15	1·14912	78·62
V.....	56·5—60·0	28·37	1·11878	72·18
VI.....	60·0—63·0	51·70	1·09150	66·04
VII.....	63·0—70·0	38·31	1·02430	49·00
VIII.....	70·0—75·0	22·44	0·97528	34·39
IX.....	75·0—78·5	27·68	0·91677	14·30
X.....	78·5—80·0	30·69	0·88733	2·84
XI.....	80·0—80·1	31·05	0·88072	0·15

Distillation with Long Tube.—The tube used in this experiment was that shown in Fig. 2. Two thermometers were placed in this tube, one (B) at the bottom, the other (G) at the top; it was thus possible to observe any change which might take place in the temperature of

the mixed vapours as they passed up the tube. 499·3 grams of a mixture having a density of 1·07660 at 19·80°, and containing therefore 62·51 per cent. of CS₂ were distilled; the barometric pressure during the distillation was 771·3 mm. The results are given in the following table:—

Number of fraction.	Temperature of distillation.		Weight of fraction.	Density at 19·80°	Percentage of CS ₂ .
	B.	G.			
I.....	53·7—54·5	50·5 —51·5	41·00	1·19528	87·65
II.....	54·5—55·5	51·5 —52·25	65·94	1·19047	86·07
III.....	55·5—57·3	52·25—53·5	73·56	1·17604	84·01
IV.....	57·3—60·0	53·5 —55·5	66·69	1·15631	80·11
V.....	60·0—63·5	55·5 —58·0	51·77	1·13432	75·54
VI.....	63·5—67·0	58·0 —61·0	31·46	1·10869	69·97
VII.....	67·0—75·5	61·0 —71·5	51·81	1·03583	52·14
VIII.....	75·5—79·5	71·5 —77·5	31·00	0·94180	23·27
IX.....	79·5—80·6	77·5 —79·7	25·10	0·89356	5·36
X.....	80·6—81·0	79·7 —80·0	28·82	0·88158	0·50

In order to compare the results of these two distillations they must be reduced to some common form; for although the original mixtures contained the same amount of CS₂ in both cases, the weights of the corresponding fractions were not equivalent. The distillations were therefore expressed graphically (see diagram) in the following simple manner:—

Let W = the total weight distilled, $w_1, w_2, w_3 \dots$ = the weights of the several fractions; then $\frac{100 w_1}{W}, \frac{100 w_2}{W}$ &c., will represent the weights of the fractions expressed in hundredths of the total weight W . Now let $y_1, y_2, y_3 \dots$ = the percentages of CS₂ in the several fractions; during the distillation of a fraction the vapour passing over varies in composition, its mean value being represented by the composition of the whole fraction = y . If we suppose that the vapour has this mean composition when exactly half the fraction has passed over, then when the accumulated distillate equals $\frac{50 w_1}{W} = x_1$ the vapour passing over will contain y_1 per cent. of CS₂; when the distillate equals $\frac{100 w_1}{W} + \frac{50 w_2}{W} = x_2$, the vapour passing over will contain y_2 per cent. of CS₂; when it equals $\frac{100 (w_1 + w_2)}{W} + \frac{50 w_3}{W} = x_3$, the vapour will contain y_3 per cent. of CS₂, and so on.

We have therefore the necessary data for determining the points of a curve expressing the variation in composition of the vapour as the distillate passes over, or in other words, the curve gives us the composition of each hundredth of the distillate.

I have included in the diagram the curves representing the two first distillations recorded in the paper previously referred to (this

Journal, 1879, Trans., 547), which were made with mixtures containing practically the same amounts of CS_2 , viz., 61.95 per cent. and 61.76 per cent. The following table gives the values of $x_1, y_1; x_2, y_2$, &c., for each of the four distillations, a representing the distillation from the retort, b that from the flask with **T**-piece, c that with dephlegmator, d that with long cooling tube:—

<i>a.</i>		<i>b.</i>		<i>c.</i>		<i>d.</i>	
<i>x.</i>	<i>y.</i>	<i>x.</i>	<i>y.</i>	<i>x.</i>	<i>y.</i>	<i>x.</i>	<i>y.</i>
2.9	82.9	3.6	81.3	4.8	87.7	4.1	87.7
14.3	81.2	14.7	82.5	19.2	84.5	14.8	86.1
28.9	78.8	29.7	79.8	34.6	81.3	28.8	84.0
43.0	75.4	42.9	76.2	47.8	78.6	42.8	80.1
55.9	70.3	53.1	72.5	57.8	72.2	54.7	75.5
65.4	64.1	62.0	66.7	65.1	66.0	63.0	70.0
72.8	56.4	69.9	59.1	73.3	49.0	71.4	52.1
78.9	45.8	76.6	49.5	78.8	39.4	79.7	23.3
81.9	30.6	83.0	33.9	83.4	14.3	85.3	5.4
89.7	15.1	88.7	16.3	88.8	2.8	90.7	0.5
93.9	5.3	93.7	4.5	94.5	0.2	—	—
95.8	0.9	98.1	0.5	—	—	—	—

On examining the four curves obtained by joining each series of points, of which the above numbers are the co-ordinates, we see, firstly, that the **T**-piece, although generally employed merely to immerse the stem of the thermometer in the vapour, was not without considerable influence on the distillation; secondly, that both the dephlegmator and the cooling tube produced much better results than the retort and the flask with **T**-piece; thirdly, that the distillation with the cooling tube was rather better than that with the dephlegmator.

Of these results the last alone calls for further examination. Strictly speaking, the comparison of the distillations c and d shows that under certain conditions better results can be obtained with a long tube than can be obtained under certain other conditions with a dephlegmator. Those who have had experience with these forms of apparatus will have observed that the rapidity with which the process of distillation is conducted largely influences the result; the amount of cooling surface also cannot be a matter of indifference. In order therefore to compare accurately the two methods, and to see whether the dephlegmator has any special value, the several distillations should be effected in the same time and with the same extent of cooling surface.

FIG. 3.

With this object in view I constructed the dephlegmator represented in Fig. 3; it consists of a glass tube 500 mm. long, and having an internal diameter of 20 mm. This tube carries nine small discs of wire gauze (40 holes to the inch), a piece of brass tube, *cd*, 2.5 mm. in bore and 45 mm. long is passed through the centre of each disc and soldered to the gauze, so that about 8 mm. of the tube project above it. The lower end of each piece of tube is deeply notched with a triangular file, and soldered into a small brass cup *d* (the heads of upholsterer's brass nails serve admirably for these cups). The lower end of the glass tube is fitted with a cork into the flask or still, to the upper end is adapted an ordinary T-piece. The tubes *cd* serve to carry away the liquid from the top of the gauze discs, the cup at the bottom answering as a trap to prevent the vapour passing up the tube instead of going through the gauze. It is essential, when No. 40 gauze is used, that these tubes should be at least 45 mm. long, as the adhesion of the

liquid to the gauze is so considerable that the pressure of the vapour underneath is sufficient to force the liquid out of a shorter tube; with finer gauze a still longer tube must, of course, be employed. In the figure the discs of copper gauze are drawn fitted into small rings of cork; this not only holds them more firmly, but also causes the whole of the condensed liquid to accumulate on their upper surfaces instead of running down the side of the glass tube; the cork would, of course, be unsuitable for liquids of high boiling point.

This dephlegmator was constructed only with a view to the ready removal of the discs, &c., so that the same tube might be used with and without them. The simple construction, the absence of fragility, and the fact that under no circumstances does it get overloaded with condensed liquid, are, however, advantages which render it preferable to those ordinarily used.

I now attempted to carry out two distillations with the same liquid in the same length of time, one with the gauze discs, the other without. I found, however, that this could not be done even when a gauge was fitted to the Bunsen burner used, and the gas maintained at a constant pressure by means of a screw clamp. Three distillations were therefore made with the discs and two without; these, as will be seen, were sufficient to show whether the two methods were identical

or not. In each case 1000 c.c. of a mixture of benzene and carbon disulphide containing about 62·7 per cent. of CS_2 was employed. The density of the benzene at $19\cdot80^\circ$ was 0·88049, that of the carbon disulphide was 1·26629; they were both carefully purified, and their densities were so nearly the same as those of the liquids previously used, viz., 0·88034 and 1·26642 that the same table of densities and percentages was employed. The distillation was continued until four fractions of 200 c.c. each had passed over; it was then stopped, and the densities of the four fractions and of the residue were observed; the results were as follows:—

I. *Distillation with gauze discs. Mixture containing 62·77 per cent. of CS_2 .*

Number of fraction.	Time occupied in distilling.	Temperature of distillation.	Density corr. to $19\cdot80^\circ$.	Percentage of CS_2 .
I	29	$^\circ$ — $51\cdot95$	1·19842	88·23
II	30	$51\cdot95$ — $54\cdot20$	1·17757	81·31
III	44	$54\cdot20$ — $60\cdot0$	1·14811	78·41
IV	97	$60\cdot0$ — $80\cdot0$	0·98993	38·78
Res.	—	— —	0·88027	00·00

II. *Distillation with gauze discs. Mixture containing 62·70 per cent. of CS_2 .*

Number of fraction.	Time occupied in distilling.	Temperature of distillation.	Density corr. to $19\cdot80^\circ$.	Percentage of CS_2 .
I	54	$^\circ$ — $50\cdot2$	1·21959	92·02
II	54	$50\cdot2$ — $52\cdot0$	1·20705	89·83
III	52	$52\cdot0$ — $67\cdot0$	1·14022	76·77
IV	95	$67\cdot0$ — $80\cdot0$	0·94429	24·15
Res.	—	— —	0·88019	00·00

III. *Distillation with gauze discs. Mixture containing 62·82 per cent. of CS_2 .*

Number of fraction.	Time occupied in distilling.	Temperature of distillation.	Density corr. to $19\cdot80^\circ$.	Percentage of CS_2 .
I	85	$^\circ$ — $50\cdot1$	1·22877	93·66
II	40	$50\cdot1$ — $53\cdot5$	1·18559	85·81
III	60	$53\cdot5$ — $62\cdot2$	1·14599	77·97
IV	73	$62\cdot2$ — $80\cdot6$	0·92097	15·85
Res.	—	— —	0·88054	00·00

IV. *Distillation with same tube without gauze. Mixture containing 62.74 per cent. of CS₂.*

Number of fraction.	Time occupied in distilling.	Temperature of distillation.	Density corr. to 19°80°.	Percentage of CS ₂ .
I	45	— — 52°·6	1·19066	86·79
II	45	52·6 — 54·9	1·17413	83·63
III	40	54·9 — 60·8	1·13420	75·52
IV	36	60·8 — 77·2	1·01833	47·31
Res.	—	— —	0·88756	2·93

V. *Distillation without gauze discs. Mixture containing 62.54 per cent. of CS₂.*

Number of fraction.	Time occupied in distilling.	Temperature of distillation.	Density corr. to 19°80°.	Percentage of CS ₂ .
I	225	— — 50°·7	1·20960	90·30
II	300	50·7 — 54·6	1·20032	88·58
III	285	54·6 — 66·1	1·14887	78·57
IV	225	66·1 — 80·5	0·93691	21·56
Res.	—	— —	0·88053	0·00

On inspecting these numbers we see, in the first place, that they afford convincing proof of the statement previously made that the rate of distillation is an element of considerable importance, showing that the slower the distillation the more carbon disulphide does the distillate contain, and that this is equally the case whether the vapours are washed or not. In comparing together the percentages of the various fractions it must, of course, be remembered that only the first fractions of each distillate are strictly comparable, for after these had passed over, the liquid in the still had no longer the same composition in each successive distillation. This explains, for instance, why the third fraction of the first distillation contained more CS₂ than that of the third, though it distilled in a shorter time. In the first case a less quantity of CS₂ had been previously removed; at the beginning of the third fraction therefore the liquid in the still was much richer in CS₂.

These distillations further prove conclusively that the processes of *washing* and of *cooling* are not identical. The fifth distillation was made under the most advantageous circumstances, that is, it was conducted at the slowest possible rate, yet the result was decidedly inferior to that of the second in which the vapour was washed, and which was completed in a fourth of the time. The same remark applies to the fifth and third, and to the fourth and first distillations. Since in equal times with equal surfaces the radiation must be the same, the effect of radiation in the fifth case must have been greater than in the second; the better result in the second case must there-

fore have been due to the presence of the gauze discs. A certain amount of secondary distillation does therefore take place in the dephlegmator, and the question whether the apparatus has any special value is answered in the affirmative.

Notwithstanding this result, we are not yet in a position to state that the dephlegmator is the best apparatus for fractional distillation, and that because we have by no means exhausted the resources of the process of *cooling*. The mixed vapours in passing up a tube may obviously be subjected to more and more radiation if the tube be gradually increased in length, until at last no vapour will reach the top of the tube; the best possible result will be obtained when the vapour just creeps over the top, before complete condensation takes place, having then reached its lowest possible temperature. It would of course be impracticable to effect distillations in this way, but the object in view is readily attained by passing the vapours through a tube or still head maintained at a given temperature, as is done every day when distillations are carried out on a manufacturing scale.

If the temperature of the still head be the lowest possible compatible with the passage of vapour into the condenser, the result will be the best which the process admits of.

The next step in this investigation was therefore to make a suitable apparatus for the above purposes, the general character of the one finally adopted is shown in Fig. 4.

The still A communicates with a coil C, terminating in a vertical portion open at the top, into which a thermometer is fitted with a cork in the usual manner; a lateral tube B serves to conduct the vapour from the coil into the condenser. The whole of the coil C, including the junction with the tube B, is enclosed in a cylindrical copper box 300 mm. long by 110 mm. in diameter.

The two ends of this cylinder are tied together by means of the copper tube *aa*, which not only strengthens the cylinder, but, being open at the top, serves for the introduction of a second thermometer, which indicates its temperature. This copper box is filled up to the level *l* with a liquid or mixture of liquids boiling at the required temperature, the heat being furnished by a ring burner, *bb*. The vapour given off by this boiling liquid passes up the tube *dd* to the condenser F, whence it returns in a liquid form by the tube *kk* to the bottom of the box E.

FIG. 4.

The small tube *m* serves as a communication with the atmosphere. As there is considerable trouble in changing from one liquid to another when a different temperature is required, the apparatus is completely closed except at *m*, by connecting *m* with an air chamber, in which any constant pressure can be conveniently maintained; the boiling point of the liquid in *E* can be altered at will. With a view to the use of the apparatus in this manner, the copper box *E* and the tubes connected with it were tested at a pressure of 100 lb. on the square inch.

In employing this apparatus, the ring burner *bb* is first lighted, when the liquid in *E* begins to boil, the temperature as indicated by the thermometer in *aa* (this tube is filled with water or petroleum) soon becomes constant, and at the same time the reading of the thermometer placed in the top of the coil ceases to vary; heat is then applied to the still *A*, and the distillation carried out as rapidly as can be done without altering the reading of the thermometer in the coil.

For the first distillation made with this apparatus, methylated spirit was put in the box *E* and the pressure maintained was such that ebullition took place at about 57°. About 800 grams of a mixture of benzene and carbon disulphide were put in the still *A*, and the distillation collected in 10 fractions.

The mixture in the still at the beginning of the distillation contained 45.00 per cent. of CS_2 ; at the end it contained 26.56 per cent. The barometric pressure during the distillation was 750.7 mm.

The thermometer *B* was placed in *aa*, the thermometer F_2 in the top of the coil. The details of the distillation were as follows:—

No. of fraction.	Reading of <i>B</i> when fraction removed.	Reading of F_2 when fraction removed.	Density of fraction at 19.80°.	Percentage of CS_2 in fraction.
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

The slight rise in the reading of F_2 towards the end of the distillation was due to the vapour passing too rapidly through the coil; it did not seem, however, to have any influence on the composition of the distillate.

A second distillation was made with 600 grams of a mixture containing 11·47 per cent. of CS_2 ; the barometric pressure was 753·1 mm. At the end of the experiment the liquid remaining in the still contained only 4·33 per cent. of CS_2 ; the details were as follows:—

No. of fraction.	Reading of B when fraction removed.	Reading of F_2 when fraction removed.	Density of fraction at 19·80°.	Percentage of CS_2 .
I	70·29	69·94	·98826	38·44
II	70·35	69·98	·98516	37·48
III	70·57	70·23	·98498	37·42
IV	70·56	70·24	·98527	37·52

These two distillations show that the composition of the distillate is independent of the amount of carbon disulphide in the still, but varies with the temperature of the coil or still head.

Two distillations were now made with the copper cylinder E filled with pure carbon disulphide, the boiling point of this liquid being evidently the lowest temperature at which any vapour given off by a mixture of benzene and carbon disulphide can pass into the condenser. In the first of these distillations a mixture containing 42·69 per cent. of CS_2 was employed, while the residue in the still when the experiment was stopped contained 32·37 per cent. of CS_2 ; the amount of CS_2 in the various fractions of the distillate was found to vary between 97·32 per cent. and 98·72 per cent. The distillate did not gradually increase or diminish in density, the higher and lower percentages following each other indiscriminately. In the second distillation for which the liquid remaining from the first was used, the liquid in the still contained at the beginning 32·37 per cent., and at the end 25·21 per cent. of CS_2 ; in this case the amount of CS_2 in the distillate varied from 97·48 per cent. to 99·19 per cent.

These two experiments show that when the still head is maintained at a temperature equal to the boiling point of the most volatile compound in a mixture, that compound alone, or nearly alone, passes over into the condenser; it is therefore possible by the use of this apparatus to effect an almost complete separation of the various constituents of a mixture of volatile substances in one distillation.

In order to show the practical value of the method, I may mention that I have frequently used it to separate benzene from the toluene and other substances which ordinary commercial benzene contains in large quantities.

The benzene thus obtained has always been nearly pure. As an example, the following rectification of some crude benzene will suffice. A sample of 200 c.c. of this liquid was distilled in an ordinary flask; it

began to distil at 85° ; at 90° 120 c.c. had accumulated in the receiver, at 95° 153 c.c., at 100° 168 c.c., at 105° 179 c.c., and at 110° 192 c.c. 1100 c.c. of this very impure liquid were distilled with the apparatus above described, maintained at a temperature of 81° ; this was rather too high to give a really good result; nevertheless 500 c.c. of rectified benzene were obtained, of which a sample of 200 c.c. distilled as follows:—Distillation commenced at 80.0° ; at 80.4° 155 c.c., at 80.8° 176 c.c., at 81.0° 180 c.c., and at 82.0° 191 c.c. had accumulated in the receiver. When 500 c.c. of this rectified benzene had passed over the experiment was stopped, and a sample of the residue distilled as follows:—Distillation commenced at 91° ; at 95° 80 c.c., at 100° 130 c.c., at 105° 158 c.c., at 110° 186 c.c. had passed into the receiver; it is therefore seen from how impure a liquid pure benzene may be directly obtained.

As regards the results contained in the above paper, it may be contended that they present but little novelty; it was, however, necessary that the effects obtained by the different methods should be exactly defined and numerically stated before a complete explanation of fractional distillation could be advanced.