On the Separation of Three Liquids by Fractional Distillation

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ducing the change, but by adding capacity to the sparking circuit the effect could be greatly modified. Replying to a question from Mr. Rimington, he said the change was due to electro-magnetic vibrations, and not to light emitted by the sparks.

Mr. Blakesley enquired if lengthening the sparks produced greater effect on the copper filings.

Mr. Lucas asked if the resistance of a tube ever became infinite again if left for a long time.

In reply, Mr. Croft said the current sometimes passed before the spark actually occurred between the knobs. He had not left tubes for very long, and had not found the resistance reappear without tapping.

XXIX. *On the Separation of Three Liquids by Fractional Distillation.* By Professor F. R. BARRELL, M.A., B.Sc., G. L. THOMAS, B.Sc., and Professor SYDNEY YOUNG, D.Sc., F.R.S., *University College, Bristol* *.

It is well known that the separation by fractional distillation of two substances which are miscible in all proportions and which do not—like propyl alcohol and water or formic acid and water—form mixtures of constant boiling-point, is usually a simple matter if there is a considerable difference in their boiling-points. The facility with which the separation can be effected depends, in fact, chiefly on this difference.

When, however, we have to deal with a mixture of three substances, the difficulty is greatly enhanced, and if the boiling-points are not far apart it may be almost, if not quite impossible to separate any quantity of the middle substance in a state of purity by the ordinary methods of fractional distillation.

The variation in the composition of the distillate from a mixture of two substances, the boiling-point of which rises constantly during the distillation, has been carefully investigated

* Read November 10, 1893.

by F. D. Brown (Trans. Chem. Soc. 1879, p. 550; 1880, pp. 49 & 304; 1881, p. 517)*; and his results may be briefly stated as follows:—Calling the relative weights of the two liquids at any instant in the still W_1 and W_2 , the relative weights at the same moment in the vapour (and therefore in the distillate at this instant coming over from the mixture $W_1 + W_2$) x_1 and x_2 , and the vapour-pressures of the pure substances at the boiling-point of the mixture, P_1 and P_2 , the composition of the instantaneous distillate is given approximately by the equation

$$\frac{x_1}{x_2} = \frac{W_1}{W_2} \cdot \frac{P_1}{P_2},$$

but by substituting a constant, c , for the ratio $\frac{P_1}{P_2}$, thus

$$\frac{x_1}{x_2} = c \cdot \frac{W_1}{W_2},$$

a still better result is obtained.

The ratio $\frac{P_1}{P_2}$ would, of course, vary to some extent during

* For an account of the experimental work and of the theoretical conclusions relating to the distillation of pairs of liquid that are (a) non-miscible, (b) miscible within limits, (c) miscible in all proportions, the article by one of us on "Distillation" in Thorpe's 'Dictionary of Applied Chemistry' may be consulted. Pairs of liquids belonging to the first and second classes boil at a lower temperature than even the more volatile component when distilled alone, and no separation can be effected by fractional distillation. Among those in the third class there are some from which only one of the two substances can be so separated; in each case of this kind there is a particular mixture (the composition of which varies to some extent with the pressure) which distils at a constant temperature without change of composition, and it is this mixture that would be separated by fractional distillation from that one of the pure substances which is present in excess. In some cases—such as propyl alcohol and water—the mixture of constant boiling-point and composition boils at a lower temperature than either of the liquids when distilled alone; in other cases—for example, formic acid and water—this mixture has a higher boiling-point than either component.

It is only when the boiling-point of every possible mixture lies between those of the components that both liquids can be separated by fractional distillation; it is only to such cases that Brown's law is applicable, and, in the case of three liquids, it is only such mixtures that are considered in this paper.

the distillation; the value of the constant, c , does not differ greatly from the mean value of the ratio $\frac{P_1}{P_2}$.

This equation of Brown's may be written in the form

$$\frac{d\xi}{d\eta} = c \frac{\xi}{\eta},$$

where ξ = residue of liquid A at any instant,

„ η = „ „ B „

Taking L and M as the weights of A and B originally present, and $L + M = 1$, we obtain by integration

$$\frac{M}{L} y \{c + (1-c)y\}^{c-1} = c^c (1-x)^{c-1} (1-y)^c,$$

where y = quantity of the more volatile liquid A in unit weight of the distillate coming over at the instant when x is the quantity of liquid distilled.

By means of this equation we may trace the changes of composition that take place in the course of a distillation, and the variation in the composition of the distillate may be represented graphically.

To take a very simple case, let us suppose that $c = 2$, and that $L = M = \frac{1}{2}$.

Fig. 1.

In the diagram (fig. 1) the amounts of distillate that have been collected are represented as abscissæ, and the relative

quantities of the two liquids A and B in the distillate at any moment as ordinates.

It will be seen that the composition of the distillate alters slowly at first, then more and more rapidly, also that while the first portion of the distillate contains a considerable amount of the less volatile substance B, the last portion is very nearly free from the lower-boiling component A. These points are fully confirmed by experiment.

By fractionating a few times in the ordinary way, collecting the distillates in six or eight fractions, we shall have a very large excess of A in the first fraction, and of B in the last.

Suppose now that we have two of these fractions, one containing A and B in the ratio of 9 : 1, and the other in the

Fig. 2.

Fig. 3.

ratio of 1 : 9, and that we distil these fractions separately and completely; the results will then be represented by figs. 2 and 3.

In making use of this formula it is assumed that no condensation (and therefore no fractionation) goes on in the still-head, but that the vapour reaches the condenser in the same state as when first evolved from the liquid in the still. It is obvious that by using a long still-head or a dephlegmator a more rapid separation would be effected.

In any case it is evident that after a sufficient number of fractionations, the first portion of the distillate from the first

fraction will be free from B, while the residue from the last fraction will be free from A.

Suppose now that our mixture contains a third substance, C, the boiling-point of which is higher than that of B.

It may be conjectured that in the progress of the distillation, the composition of the distillate at any instant will be analogous to that determined experimentally by Brown in the case of two liquids: namely, "the proportion of the three substances in the vapour forming the instantaneous distillate is the same as that of the weights of the three substances in the residue in the still, each weight being multiplied by a suitable constant which is roughly proportional to the vapour-pressure of the corresponding liquid."

With this assumption it is easy, as in the case of two liquids, to calculate curves representing graphically the progress of the distillation.

Let ξ, η, ζ = weights of the three liquids in the still at any instant;

$\therefore d\xi, d\eta, d\zeta$ = weights of the three substances in the instantaneous distillate.

By hypothesis,

$$\frac{d\xi}{a\xi} = \frac{d\eta}{b\eta} = \frac{d\zeta}{c\zeta}.$$

Integrate

$$\frac{1}{a} \log \xi = \frac{1}{b} \log \eta + k = \frac{1}{c} \log \zeta + k'.$$

Let L, M, N be the original weights of the three liquids, and ($L + M + N = 1$);

$$\therefore \frac{1}{a} \log L = \frac{1}{b} \log M + k = \frac{1}{c} \log N + k'.$$

Subtract

$$\frac{1}{a} \log \frac{\xi}{L} = \frac{1}{b} \log \frac{\eta}{M} = \frac{1}{c} \log \frac{\zeta}{N};$$

$$\therefore \left(\frac{\xi}{L}\right)^{\frac{1}{a}} = \left(\frac{\eta}{M}\right)^{\frac{1}{b}} = \left(\frac{\zeta}{N}\right)^{\frac{1}{c}}.$$

Let

$$\left. \begin{array}{l} y_1 = \text{weight of A} \\ y_2 = \text{,, B} \\ y_3 = \text{,, C} \end{array} \right\} \begin{array}{l} \text{in unit weight of distillate} \\ \text{coming over when } x = \text{weight} \\ \text{of liquid distilled;} \end{array}$$

$$\therefore y_1 = \frac{d\xi}{d\xi + d\eta + d\zeta} = \frac{a\xi}{a\xi + b\eta + c\zeta};$$

$$y_2 = \frac{b\eta}{a\xi + b\eta + c\zeta}; \quad y_3 = \frac{c\zeta}{a\xi + b\eta + c\zeta}.$$

Let

$$\frac{\xi}{N} = z, \quad \frac{a}{c} = \lambda + 1, \quad \frac{b}{c} = \mu + 1;$$

$$\therefore \xi = Lz^{\lambda+1}, \quad \eta = Mz^{\mu+1}, \quad \zeta = Nz;$$

$$\therefore 1 - x = \xi + \eta + \zeta = Lz^{\lambda+1} + Mz^{\mu+1} + Nz;$$

$$y_1 = \frac{aLz^{\lambda}}{aLz^{\lambda} + bMz^{\mu} + cN}; \quad y_2 = \frac{bMz^{\mu}}{aLz^{\lambda} + bMz^{\mu} + cN};$$

$$y_3 = \frac{cN}{aLz^{\lambda} + bMz^{\mu} + cN}.$$

The elimination of z from the expressions for x and y is impracticable, but the curves may be readily traced by treating z as an independent variable.

In the following curves (figs. 4 & 5) we have taken

$$a=4, \quad b=2, \quad c=1, \quad [\text{and } \therefore \lambda=3, \mu=1],$$

these being nearly proportional to the vapour-pressures of methyl, ethyl, and propyl acetates.

I. represents the first distillation; in it $L=M=N=\frac{1}{3}$. II. α , II. β , II. γ , II. δ , II. ϵ represent what would take place if the five fractions into which I. is divided were separately distilled; the composition of these fractions being found from the curves I. to be:—

	A or L.	B or M.	C or N.
II. α	·543	·300	·157
II. β	·47	·33	·20
II. γ	·37	·365	·265
II. δ	·22	·39	·39
II. ϵ	·047	·265	·687

Fig. 4.

It is to be noted that in II. α , which is richest in the low-boiling liquid A, the amount of A rises from $\cdot543$ to an initial value $\cdot74$, and in the first half (or at least $\frac{2}{3}$) of the distillate the aggregate amount of A rises to $\cdot7$.

In II. ϵ , which is richest in the high-boiling liquid C, the amount of C rises from $\cdot687$ to about $\cdot9$ in the last fifth, or $\cdot82$ in the last two-fifths of the distillate; whereas in II. δ ,

Fig. 5.

which is richest in B, the middle liquid, the amount of B rises merely from $\cdot39$, its initial value, to about $\cdot45$, its value

for the fifth which is collected just after the first half ($\cdot 5$ to $\cdot 7$). It is curious that in each of these distillations B rises to practically the same maximum value, viz. $\cdot 45$, the effect of the varying richness of the fractions in regard to B being merely to widen out or contract the B curve.

III. αa , III. δ " cd ," III. ϵe represent the distillation of those fractions of II. which are richest in A, B, and C respectively, and give some indication of the processes going on at the important stages of the third fractionation. In these A rises from $\cdot 7$ to $\cdot 82$, B from $\cdot 45$ to $\cdot 5$, C from $\cdot 9$ to $\cdot 98$. Here we notice that, owing to the small amount of C present in III. αa (whose original composition is A $\cdot 696$, B $\cdot 239$, and C $\cdot 065$), B attains a higher maximum ($\cdot 525$) than it does ($\cdot 496$) in III. δcd , which is far richer in B originally [A $\cdot 182$, B $\cdot 44$, C $\cdot 378$].

P represents a distillation at an advanced stage of the fractionations—of a fraction rich in B. Its initial composition is A $\cdot 02$, B $\cdot 96$, C $\cdot 02$. B is only advanced from $\cdot 96$ to $\cdot 97$ at the most favourable part of the curve, and is nowhere very free from C; this points to the difficulty of obtaining B in a pure state by the ordinary method of fractionation.

The calculations for III. δcd are appended as a specimen of the system employed (see table opposite): with the aid of the slide-rule they are very quickly effected.

Apart from the consideration of the above hypothesis and formulæ, it is clear that after five or six fractional distillations, carried out in the ordinary manner (but with a larger number of fractions than when only two substances are present), the first fraction will contain a large excess of A, a little of B, but very little, if any, of C; the middle fraction will contain an excess of B with moderate quantities of both A and C; the last fraction will consist almost entirely of C, the quantity of A, if present at all, being much smaller than that of B.

Now let us suppose that these fractions are distilled separately and completely. The first portion of the distillate from the first fraction will consist of A in a nearly pure state, and, even if it contains a little of B, will be free from C. Of

$$L = .182. \quad 1-x = .182z^4 + .44z^2 + .378z;$$

$$M = .44.$$

$$N = .378. \quad y_3 = \frac{378}{378 + 880z + 728z^3}.$$

$z.$	$.378z.$	$.44z^2.$	$.182z^4.$	$1-x.$	880 $z.$	728 $z^3.$	Denominator.	$y_3.$	$y_2.$	$y_1.$
0	0	0	0	0	0	0	378	1	0	0
.1	.038	.004	.000	.042	88	1	467	.810	.188	.002
.2	.075	.018	.000	.093	176	6	560	.675	.314	.011
.3	.114	.040	.001	.155	264	20	662	.571	.399	.030
.4	.151	.070	.005	.226	352	46	776	.488	.453	.059
.5	.189	.110	.011	.310	440	91	909	.416	.484	.100
.6	.227	.158	.024	.409	528	157	1063	.356	.436	.148
.7	.265	.216	.044	.525	616	249	1243	.304	.495	.200
.8	.303	.282	.074	.659	704	373	1455	.260	.483	.256
.9	.340	.356	.119	.815	792	530	1700	.222	.466	.312
1.0	.378	.440	.182	1.000	880	728	1986	.190	.443	.367

the middle fraction the middle portion (or probably a rather later one) will be purest, but will contain a little of both A and C. The purest part of the last fraction will be the last portion (the residue in the still) and will be quite free from A though it may contain a little of B.

By proceeding with the fractionation in the usual manner we could obtain A and C in a pure state by separating each time the first small portion of the first distillate and the residue from the last distillate : but we should have to carry the fractionation a very great deal farther before we could obtain B in a state of purity. We should, in fact, have to reduce the quantities of A and C in this fraction until they both disappeared from the middle portion of the distillate, and an idea of the difficulty of attaining such a result may be gathered from the diagram P.

With substances whose boiling-points are not very far apart the rise of temperature during such a distillation would be almost imperceptible, and in the fractionation it would be necessary to collect a large number of fractions above and below the true boiling-point of B with very small temperature-ranges. It would be necessary also to read the temperature with extreme care, and to make very accurate corrections for changes of the barometer (which would be impossible unless the vapour-pressures of the substance had previously been determined).

It has been pointed out, however, that after the mixture has been fractionated a few times, the first portion of the first distillate is free from C, while the residue from the last distillate is free from A. If, therefore, after the fifth or sixth fractionation we remove these first and last portions each time, we shall gradually accumulate two quantities of liquid, one (the first portions) containing only A and B, the other (the residues) only B and C, and these may be separately fractionated in the ordinary way.

It is to be noticed also that as a quantity of liquid is removed each time, the total amount to be distilled, and therefore the time required for the distillation, gradually diminishes.

In arranging the fractions—as regards temperature—it is

advisable, if the true boiling-points of the liquids are known, to take these temperatures and also the middle temperatures between the boiling-points of A and B and of B and C as definite points, and to arrange the fractions as far as possible symmetrically about these points. There will thus be fractions of small and diminishing temperature-range above and below the boiling-point of B—and at the boiling-points of A and C after a few fractionations and until these substances are to a large extent eliminated—and fractions of large and increasing temperature-range above and below the two middle temperatures.

As the preliminary fractionation proceeds, more and more of A and C will be eliminated, so that after a time the boiling-point of the first portion of the lowest fraction will gradually rise, while that of the residue from the last fraction will gradually fall until either A or C disappear, or, if we proceed still further, until we have nothing but B left. Much time may therefore be saved if, instead of adding all the first portions of the lowest fractions together (and the same remark applies to the residues from the last fractions), we collect them in six or more different quantities. The final fractionations will then be in a forward state when the preliminary one is completed.

We shall in this manner obtain two quantities of B, one by the final fractionation of the first portions of the distillates from the lowest fractions of the preliminary fractionations, the other by that of the residues from the preliminary fractionations, and we can test the purity of the substance by comparing the boiling-points and the specific gravities of the two samples so obtained.

In order to test the value of this method, a mixture of 200 cub. cent. of methyl acetate (B.P. 57.1), 250 cub. cent. of ethyl acetate (B.P. 77.15), and 200 cub. cent. of propyl acetate* (B.P. 101.55) was distilled from a flask provided

* The esters had previously been purified with great care, and were distilled separately from phosphorus pentoxide immediately before being mixed. Special precautions were also taken to avoid absorption of moisture during the fractionations. The methods of preparation and purification and proofs of the purity of the esters are fully described in the *Trans. Chem. Soc.* lxiii. p. 1194.

with a still-head one metre in length. The distillate was collected in four approximately equal fractions, numbered 5, 8, 11, and 14 under F in the table (I.) below. The observed temperatures (reduced to 760 millim.), the range of temperature for each fraction (Δt), the weight of each fraction (Δw), and the ratio of the weight to the temperature-range ($\frac{\Delta w}{\Delta t}$) are also given in the tables. The second fractionation (II.) was carried out in the following manner:—the first fraction from I. (No. 5, B. P. $63^{\circ}8$ to $71^{\circ}3$) was distilled and the distillate collected in a separate receiver (No. 4) until the temperature rose to $63^{\circ}8$ *, when receiver No. 5 was substituted for it and the distillation continued until the temperature rose to $71^{\circ}0$. The gas was then turned out, and the second fraction from I. (No. 8, B. P. $71^{\circ}3$ to $77^{\circ}8$) added to the residue in the flask. Heat was again applied and the distillate collected in receiver No. 5 until the temperature again rose to $71^{\circ}0$, when it was replaced by receiver No. 8, and the distillation was continued until the temperature rose to $77^{\circ}1$. The third fraction from I. (No. 11, B. P. $77^{\circ}8$ to $89^{\circ}2$) was then added to the residue in the flask, and the distillate collected in No. 8 until the temperature again rose to $77^{\circ}1$, when No. 11 was put in its place. When the temperature had risen to $84^{\circ}4$ a new receiver, No. 13, was substituted for No. 11, and the distillation was continued until the thermometer registered $91^{\circ}7$. The last fraction from I. (No. 14, B.P. above $89^{\circ}2$) was then added to the residue in the flask and the distillate collected in No. 13 until the temperature rose again to $91^{\circ}7$, after which fractions were collected in No. 14 from $91^{\circ}7$ to $98^{\circ}4$, and No. 15 from $98^{\circ}4$ to $101^{\circ}5$, when the distillation was stopped, and the residue poured into receiver No. 17.

* The actual temperature was $63^{\circ}5$, the barometric pressure being 751.1 millim.; the value of $\frac{dp}{dt}$ at the boiling-point is 27 millim. per degree for methyl acetate, 25 millim. for ethyl acetate, and 23 millim. for propyl acetate. All the temperatures are corrected to 760 millim. by means of these constants.

VII.					VIII.				
F.	t corr. to 760 mm.	Δt .	Δw .	$\frac{\Delta w}{\Delta t}$.	F.	t corr. to 760 mm.	Δt .	Δw .	$\frac{\Delta w}{\Delta t}$.
1.	$\overset{\circ}{57.05} - \overset{\circ}{57.25}$	$\overset{\circ}{0.2}$	13.3	66.5	A ...	$\overset{\circ}{57.15} - \overset{\circ}{57.35}$	$\overset{\circ}{0.2}$	6.0	
2.	$\overset{\circ}{57.25} - \overset{\circ}{58.15}$	0.9	42.9	47.7	1.	$\overset{\circ}{57.35} - \overset{\circ}{58.25}$	0.9	11.7	58.5
3.	$\overset{\circ}{58.15} - \overset{\circ}{60.0}$	1.85	47.5	25.0	2.	$\overset{\circ}{58.25} - \overset{\circ}{60.15}$	1.9	49.1	54.6
4.	$\overset{\circ}{60.0} - \overset{\circ}{63.8}$	3.8	43.5	11.4	3.	$\overset{\circ}{60.15} - \overset{\circ}{63.8}$	3.65	45.4	23.9
5.	$\overset{\circ}{63.8} - \overset{\circ}{70.75}$	6.95	45.9	6.7	4.	$\overset{\circ}{63.8} - \overset{\circ}{70.7}$	6.9	36.0	9.5
7.	$\overset{\circ}{70.75} - \overset{\circ}{75.8}$	5.05	42.7	8.4	5.			37.8	5.5
8.	$\overset{\circ}{75.8} - \overset{\circ}{77.2}$	1.4	45.0	32.1	7.	$\overset{\circ}{70.7} - \overset{\circ}{75.8}$	5.1	41.9	8.2
11.	$\overset{\circ}{77.2} - \overset{\circ}{78.3}$	1.1	37.8	34.4	8.	$\overset{\circ}{75.8} - \overset{\circ}{77.15}$	1.35	43.8	32.4
12.	$\overset{\circ}{78.3} - \overset{\circ}{82.1}$	3.8	41.1	10.8	11.	$\overset{\circ}{77.15} - \overset{\circ}{78.2}$	1.05	51.1	48.7
13.	$\overset{\circ}{82.1} - \overset{\circ}{90.15}$	8.05	23.4	2.9	12.	$\overset{\circ}{78.2} - \overset{\circ}{81.1}$	2.9	34.1	11.8
14.	$\overset{\circ}{90.15} - \overset{\circ}{98.45}$	8.3	22.3	2.7	13.	$\overset{\circ}{81.1} - \overset{\circ}{90.05}$	8.95	22.8	2.5
15.	$\overset{\circ}{98.45} - \overset{\circ}{100.95}$	2.5	17.6	7.0	14.	$\overset{\circ}{90.05} - \overset{\circ}{98.5}$	8.45	17.8	2.1
16.	$\overset{\circ}{100.95} - \overset{\circ}{101.45}$	0.5	24.3	48.6	15.	$\overset{\circ}{98.5} - \overset{\circ}{101.0}$	2.5	16.7	6.7
17.	$\overset{\circ}{101.45} - \overset{\circ}{101.55}$	0.1	23.7	237.0	16.	$\overset{\circ}{101.0} - \overset{\circ}{101.45}$	0.45	19.4	43.3
Z ...			80.2		17.	$\overset{\circ}{101.45} - \overset{\circ}{101.55}$	0.1	12.6	126.0
			551.2		Z ...			101.5	
								547.7	
IX.					X.				
A ...	$\overset{\circ}{57.0} - \overset{\circ}{57.25}$	$\overset{\circ}{0.25}$	11.4		A ...	$\overset{\circ}{57.1} - \overset{\circ}{57.25}$	$\overset{\circ}{0.15}$	21.5	
1.	$\overset{\circ}{57.25} - \overset{\circ}{58.0}$	0.75	18.6	74.4	1.	$\overset{\circ}{57.25} - \overset{\circ}{57.75}$	0.5	16.7	111.3
2.	$\overset{\circ}{58.0} - \overset{\circ}{59.75}$	1.75	44.5	59.3	2.	$\overset{\circ}{57.75} - \overset{\circ}{59.35}$	1.6	35.7	64.9
3.	$\overset{\circ}{59.75} - \overset{\circ}{63.75}$	4.0	41.4	23.0	3.	$\overset{\circ}{59.35} - \overset{\circ}{63.75}$	4.4	43.0	26.9
4.	$\overset{\circ}{63.75} - \overset{\circ}{71.0}$	7.25	35.1	8.8	4.	$\overset{\circ}{63.75} - \overset{\circ}{71.3}$	7.55	34.9	7.9
5.			30.4	4.2	5.			28.9	3.8
7.	$\overset{\circ}{71.0} - \overset{\circ}{75.95}$	4.95	39.9	8.0	7.	$\overset{\circ}{71.3} - \overset{\circ}{76.1}$	4.8	36.9	7.7
8.	$\overset{\circ}{75.95} - \overset{\circ}{77.15}$	1.2	47.9	39.9	8.	$\overset{\circ}{76.1} - \overset{\circ}{77.15}$	1.05	57.3	54.6
11.	$\overset{\circ}{77.15} - \overset{\circ}{78.05}$	0.9	57.9	64.3	11.	$\overset{\circ}{77.15} - \overset{\circ}{77.9}$	0.75	53.9	71.9
12.	$\overset{\circ}{78.05} - \overset{\circ}{80.55}$	2.5	27.1	10.8	12.	$\overset{\circ}{77.9} - \overset{\circ}{79.9}$	2.0	23.3	11.7
13.	$\overset{\circ}{80.55} - \overset{\circ}{89.9}$	9.35	20.4	2.2	13.	$\overset{\circ}{79.9} - \overset{\circ}{89.9}$	10.0	19.8	2.0
14.	$\overset{\circ}{89.9} - \overset{\circ}{98.85}$	8.95	14.1	1.6	14.	$\overset{\circ}{89.9} - \overset{\circ}{99.3}$	9.4	12.5	1.3
15.	$\overset{\circ}{98.85} - \overset{\circ}{101.05}$	2.2	12.8	5.8	15.	$\overset{\circ}{99.3} - \overset{\circ}{101.1}$	1.8	9.7	5.4
16.	$\overset{\circ}{101.05} - \overset{\circ}{101.45}$	0.4	9.8	24.5	16.	$\overset{\circ}{101.1} - \overset{\circ}{101.5}$	0.4	8.4	21.0
17.	$\overset{\circ}{101.45} - \overset{\circ}{101.55}$	0.1	6.3	63.0	17.	$\overset{\circ}{101.5} - \overset{\circ}{101.55}$	0.05	3.5	70.0
Z ...			124.6		Z ...			132.6	
			542.2					538.6	

XI.					XII.				
F.	<i>t.</i> corr. to 760 mm.	$\Delta t.$	$\Delta w.$	$\frac{\Delta w.}{\Delta t}$	F.	<i>t.</i> corr. to 760 mm.	$\Delta t.$	$\Delta w.$	$\frac{\Delta w.}{\Delta t}$
A ...	° °	°			A ...	° °	°		
1.	57.1 - 57.2	0.1	31.5	152.0	1.	57.1 - 57.2	0.1	41.1	170.0
2.	57.2 - 57.7	0.5	34.6	69.2	2.	57.2 - 57.65	0.45	30.5	67.8
3.	57.7 - 59.1	1.4	36.4	26.0	3.	57.65 - 58.9	1.25	30.3	24.2
4.	59.1 - 63.4	4.3	34.1	7.9	4.	58.9 - 63.5	4.6	31.0	6.7
5.	63.4 - 71.5	8.1	23.9	3.0	5.	63.5 - 71.9	8.4	23.8	2.8
7.	71.5 - 76.25	4.75	36.1	7.5	7.	71.9 - 76.45	4.55	32.9	7.1
8.	76.25 - 76.95	0.7	28.5	40.7	8.	76.45 - 77.0	0.55	30.5	55.5
9.	76.95 - 77.15	0.2	27.9	139.5	9.	77.0 - 77.15	0.15	27.6	184.0
10.	77.15 - 77.35	0.2	28.7	143.5	10.	77.15 - 77.3	0.15	36.2	241.3
11.	77.35 - 77.75	0.4	29.4	73.5	11.	77.3 - 77.6	0.3	25.6	85.3
12.	77.75 - 79.35	1.6	21.9	13.7	12.	77.6 - 78.85	1.25	18.7	14.9
13.	79.35 - 89.3	9.95	18.7	1.9	13.	78.85 - 88.9	10.05	17.9	1.8
14.	89.3 - 99.55	10.25	10.9	1.1	14.	88.9 - 99.55	10.65	9.5	0.9
15.	99.55 - 101.15	1.6	9.5	5.9	15.	99.55 - 101.15	1.6	8.1	5.1
16.	101.15 - 101.45	0.3	6.0	20.0	X ...			7.8	
Y ...			8.1		(Y & Z.)	}		140.7	
Z ...			132.6						
			534.0					529.2	
XIII.					XIV.				
A ...	° °	°			A ...	° °	°		
1.	57.1 - 57.2	0.1	50.4	204.0	1.	57.1 - 57.2	0.1	60.7	147.0
2.	57.2 - 57.6	0.4	22.9	57.2	2.	57.2 - 57.6	0.4	23.6	59.0
3.	57.6 - 58.7	1.1	26.0	23.6	3.	57.6 - 58.6	1.0	22.6	22.6
4.	58.7 - 63.8	5.1	30.8	6.0	4.	58.6 - 64.25	5.65	29.9	5.3
5.	63.8 - 72.35	8.55	21.3	2.5	5.	64.25 - 72.8	8.55	18.8	2.2
7.	72.35 - 76.65	4.3	35.2	8.2	7.	72.8 - 76.65	3.85	28.8	7.5
8.	76.65 - 77.05	0.4	23.2	58.0	8.	76.65 - 77.05	0.4	27.1	67.7
9.	77.05 - 77.15	0.1	33.1	331.0	9.	77.05 - 77.15	0.1	35.2	352.0
10.	77.15 - 77.25	0.1	38.0	380.0	10.	77.15 - 77.25	0.1	43.1	431.0
11.	77.25 - 77.5	0.25	21.5	86.0	11.	77.25 - 77.45	0.2	15.6	78.0
12.	77.5 - 78.5	1.0	17.6	17.6	12.	77.45 - 78.2	0.75	17.4	23.2
13.	78.5 - 88.7	10.2	18.7	1.8	13.	78.2 - 84.7	6.5	16.0	2.4
14.	88.7 - 99.7	11.0	9.3	0.8	V ...			11.4	
W ...			8.1		(W to Z.)	}		156.6	
(X to Z.)	}		148.5					521.5	
			525.0						

XV.					XVI.				
F.	t corr. to 760 mm.	Δt .	Δw .	$\frac{\Delta w}{\Delta t}$.	F.	t corr. to 760 mm.	Δt .	Δw .	$\frac{\Delta w}{\Delta t}$.
A ...	°	°	70.1		A ...	°	°	79.9	
1.	57.1 -57.2	0.1	16.3	163.0	1.	57.1 -57.2	0.1	14.6	146.0
2.	57.2 -57.6	0.4	21.0	52.5	2.	57.2 -57.6	0.4	17.3	43.2
3.	57.6 -58.6	1.0	17.1	17.1	3.	57.6 -58.6	1.0	14.6	14.6
4.	58.6 -64.8	6.2	27.1	4.4	4.	58.6 -65.35	6.75	25.0	3.7
5.	64.8 -73.4	8.6	17.4	2.0	5.	65.35-73.9	8.55	15.6	1.8
7.	73.4 -76.7	3.3	27.8	8.4	7.	73.9 -76.8	2.8	26.6	9.2
8.	76.7 -77.05	0.35	21.7	62.0	8.	76.8 -77.1	0.3	26.7	89.0
9.	77.05-77.15	0.1	43.0	430.0	9.	77.1 -77.15	0.05	39.0	780.0
10.	77.15-77.2	0.05	40.4	808.0	10.	77.15-77.2	0.05	39.9	798.0
11.	77.2 -77.4	0.2	21.2	106.0	11.	77.2 -77.35	0.15	24.4	162.6
12.	77.4 -78.0	0.6	12.5	20.8	12.	77.35-77.9	0.55	11.6	21.1
13.	78.0 -79.6	1.6	9.7	6.1	U ...			6.6	
V ...			15.8		(V to Z.)			172.4	
(W to Z.)			156.6					514.2	
			517.7						
XVII.					XVIII.				
A ...	°	°	86.7		A ...	°	°	94.1	
1.	57.1 -57.2	0.1	14.4	144.0	1.	57.1 -57.2	0.1	11.3	113.0
3.	57.2 -57.6	0.4	14.3	35.7	2.	57.2 -57.6	0.4	13.4	33.5
3.	57.6 -58.6	1.0	13.5	13.5	3.	57.6 -58.6	1.0	10.7	10.7
4.	58.6 -65.8	7.2	22.4	3.1	4.	58.6 -66.25	7.65	21.3	2.8
5.	65.8 -74.4	8.6	15.9	1.8	5.	66.25-74.85	8.7	15.0	1.7
7.	74.4 -76.85	2.45	24.7	10.1	7.	74.85-76.85	2.0	21.4	10.7
8.	76.85-77.1	0.25	19.0	76.0	8.	76.85-77.1	0.25	20.5	82.0
9.	77.1 -77.15	0.05	38.3	766.0	9.	77.1 -77.15	0.05	41.2	814.0
10.	77.15-77.2	0.05	48.0	960.0	10.	77.15-77.2	0.05	49.6	992.0
11.	77.2 -77.3	0.1	22.0	220.0	11.	77.2 -77.3	0.1	21.0	210.0
12.	77.3 -77.65	0.35	9.6	27.5	T ...			6.0	
U ...			10.2		(U to Z.)			182.6	
(V to Z.)			172.4					508.1	
			511.4						
XIX.					XX.				
A ...	°	°	100.3		A ...	°	°	105.5	
1.	57.1 -57.2	0.1	9.5	95.0	1.	57.1 -57.15	0.05	5.9	118.0
2.	57.2 -57.6	0.4	11.7	29.2	2.	57.15-57.55	0.4	10.7	26.7
3.	57.6 -58.6	1.0	9.0	9.0	3.	57.55-58.55	1.0	8.9	8.9
4.	58.6 -66.75	8.15	19.0	2.3	4.	58.55-67.25	8.7	17.6	2.0
5.	66.75-75.35	8.6	15.7	1.8	5.	67.25-75.95	8.7	16.6	1.9
7.	75.35-76.85	1.5	18.4	12.3	7.	75.95-76.95	1.0	16.0	16.0
8.	76.85-77.1	0.25	18.3	73.2	8.	76.95-77.15	0.2	13.4	67.0
9.	77.1 -77.15	0.05	39.5	790.0	9.	77.15	0.05 {	45.0	1888.0
10.	77.15-77.2	0.05	57.6	1152.0	10.	to 77.2		49.4	
11.	77.2 -77.3	0.1	13.9	139.0	11.	77.2 -77.25	0.05	13.0	260.0
T ...			9.7		S ...			8.6	
(U to Z.)			182.6		(T to Z.)			192.3	
			505.2					502.9	

XXI.					XXII.				
F.	<i>t</i> corr. to 760 mm.	Δt .	Δw .	$\frac{\Delta w}{\Delta t}$.	F.	<i>t</i> corr. to 760 mm.	Δt .	Δw .	$\frac{\Delta w}{\Delta t}$.
A ...	°	°	105.5		(A & B.)	°	°	117.1	
B ...	-57.15		11.6		C ...	-57.55		10.1	
2.	57.15-57.55	0.4	7.2	18.0	3.	57.55-58.55	1.0	6.0	6.0
3.	57.55-58.55	1.0	7.0	7.0	4.	58.55-67.2	8.65	12.6	1.5
4.	58.55-67.2	8.65	16.3	1.8	5.	67.2-76.5	9.3	19.2	2.1
5.	67.2-76.3	9.1	18.2	2.0	7.	76.5-77.05	0.55	15.4	28.0
7.	76.3-77.0	0.7	11.2	16.0	8.	77.05-77.15	0.1	21.5	215.0
8.	77.0-77.15	0.15	25.3	168.6	9.	77.15 { slight rise. } very high	0 {	24.0	} very high
9.	77.15 { slight rise	0.0	38.7	} very high	10.			36.6	
10.			35.5		11.			17.3	
11.	77.15-77.2	0.05	14.8	296.0	R ...			9.1	
S ...			16.8		(S to Z.)			209.1	
(T to Z.)			192.3					498.0	
			500.4						

XXIII.					XXIV.				
(A to C.)	°	°	127.2		(A to C.)	°	°	127.2	
D ...	-58.55		8.6		D ...	-58.55		10.0	
4.	58.55-67.2	8.65	9.1	1.1	4.	58.55-67.2	8.65	6.8	0.8
5.	67.2-76.7	9.4	21.7	2.3	5.	67.2-75.3	8.1	15.1	1.9
7.	76.7-77.1	0.4	14.4	36.0	6.	75.3-76.8	1.5	7.8	5.2
8.	77.1-77.15	0.05	16.6	332.0	7.	76.8-77.1	0.3	12.2	40.7
9.	77.15	0	33.1	} very high	8.	77.1-77.15	0.05	14.6	292.0
10.			25.2		9.	77.15	0	31.9	} very high
11.			77.15		11.5	10.	26.9		
R ...			19.7		Q ...			13.1	
(S to Z.)			209.1		(R to Z.)			228.8	
			496.2					494.4	

XXV.					XXVI.				
(A to D.)	°	°	137.2		(A to D.)	°	°	137.2	
E ...	-67.9		10.2		E ...	-68.9		11.9	
5.	67.9-75.5	7.6	9.3	1.3	5.	68.9-75.7	6.8	7.1	1.0
6.	75.5-76.85	1.35	9.0	6.7	6.	75.7-76.9	1.2	10.4	8.7
7.	76.85-77.1	0.25	13.2	52.8	7.	76.9-77.1	0.2	15.4	77.0
8.	77.1-77.15	0.05	20.2	404.0	8.	77.1-77.15	0.05	16.4	328.0
9.	77.15	0	21.6	} very high	9.	77.15	0	19.2	} very high
10.			19.1		10.			12.1	
Q ...					23.2			Q ...	
(R to Z.)			228.8		(R to Z.)			228.8	
			492.3					490.8	

The third fractionation (III.) was carried out in a similar manner, a new fraction No. 3 being collected at the beginning. As the temperature rose to $101^{\circ}55$, the true B.P. of propyl acetate, before the end of the last distillation, the residue in the flask consisted of this substance in a nearly pure state, and it was therefore collected in a separate flask Z, and was not redistilled during the preliminary fractionations. The residues from the subsequent fractionations up to the tenth were collected in Z, but after this, as a large amount of propyl acetate had been removed, the temperature did not reach $101^{\circ}55$, and the residue from the eleventh fractionation (B. P. above $101^{\circ}45$) was collected in a new flask, Y.

At the end of the twelfth fractionation the temperature rose only to $101^{\circ}15$, and the residue was therefore placed in a third flask, X, and subsequently the residues were collected in W, V, &c., to Q, as shown in the tables.

It was not until the fifth fractionation that the first fraction began to boil at $57^{\circ}1$, the B.P. of methyl acetate, and it was not thought advisable to separate the first portion of the first distillate until the eighth fractionation. This portion and also the corresponding ones up to the twentieth fractionation were collected together in flask A, after which the first portions were collected in B, C, D, and E.

The ratios $\frac{\Delta w}{\Delta t}$ give an indication of the purity of the various distillates, for with a pure substance, since $\Delta t=0$, $\frac{\Delta w}{\Delta t} = \infty$, while with a very impure substance there is a rapid rise of temperature during distillation, and $\frac{\Delta w}{\Delta t}$ is consequently small.

It will be seen that the ratio for the highest fraction rises rapidly, being 197 in the third fractionation and rising to 340 in the sixth, after which it diminishes again owing to removal of propyl acetate in the residues. The value for the lowest fraction increases much more slowly, reaching a maximum of 204 in the thirteenth fractionation, and afterwards diminishing owing to removal of methyl acetate.

The presence of the middle substance, ethyl acetate, is not clearly shown until the fourth fractionation, when the value of $\frac{\Delta w}{\Delta t}$ for the sixth distillate (No. 9) is higher than for those above and below it; but the gradual accumulation of the ethyl acetate in the middle fractions in subsequent fractionations is clearly shown by the rise in the values of $\frac{\Delta w}{\Delta t}$ for fractions 8 and 11, and after the tenth fractionation in fractions 9 and 10. The range of temperature for fractions 9 and 10 was gradually diminished from $0^{\circ}2$ each in the eleventh fractionation until no rise could be detected; there was indeed no perceptible rise of temperature during the collection of No. 11 in the twenty-second and twenty-third fractionations. It was therefore certain that after the twenty-sixth fractionation the tenth fraction was free from propyl acetate, and that the remaining fractions Nos. 5 to 10 contained only methyl and ethyl acetates.

The preliminary series of fractionations was therefore completed, no fraction now containing more than two substances.

The progress of the separation is well seen by mapping the temperatures against the total weight of distillate collected. The curves I. to XII. represent the first twelve fractionations, the weight of distillate being given in each case as percentages. The dotted lines at the extremities of the later curves represent the methyl and propyl acetates removed in the first portions of the first distillates and in the residues.

The presence of the middle substance is clearly indicated in the fourth curve, but not in the earlier ones.

Fig. 6.

I.

II.

III.

IV.

V.

VI.

VII.

VIII.

IX.

X.

XI.

XII.

Final Fractionations.

The fractions into which the esters had been separated at the end of the 26th preliminary fractionation are given below :—

Methyl and Ethyl Acetates.			Ethyl and Propyl Acetates.		
Frac-tion.	Temperature range.	Weight.	Frac-tion.	Temperature range.	Weight.
A ...	57·1	105·5	Q ...	77·15	32·3
B ...	below 57·15	11·6	R ...	above 77·15	19·7
C ...	" 57·55	10·1	S.....	" 77·2	16·8
D ...	" 58·55	10·0	T.....	" 77·3	9·7
E ...	" 68·9	11·9	U ...	" 77·65	10·2
5 ...	68·9-75·7	7·1	V ...	" 79·6	15·8
6 ...	75·7-76·9	10·4	W ...	" 99·7	8·1
7 ...	76·9-77·1	15·4	X ...	" 101·15	7·8
8 ...	77·1-77·15	16·4	Y ...	" 101·45	8·1
9 ...	77·15	19·2	Z ...	" 101·55	132·6
10 ...	77·15	12·1			
		229·7			261·1

The total weight was 490·8, so that 86 grams had been lost by evaporation and through adherence to the flasks and to the funnel through which the liquid was poured into the still.

The final separation of the esters was carried out in the following manner :—

Ethyl Acetate (1).—The fractions 5 to 10 consisted of ethyl acetate with some methyl acetate. The final fractionations in this case were a continuation of the preliminary ones and were carried out in the same manner. No. 10 was almost if not quite pure ethyl acetate, and was only distilled once more; the first portion was collected in No. 9, and the residue was taken as pure. In the remaining six fractionations the residue, after the distillation of No. 9, was each time taken as pure, and the total amount of ethyl acetate thus obtained was 56·1 grams.

Ethyl Acetate (2).—The flasks Q to U contained ethyl acetate with some propyl acetate. In the six fractionations, which were carried out in the usual way, the first portion of the distillate from Q was each time taken as pure, the small

residue in the still being rejected. The weight of pure ethyl acetate obtained from this series was 62.7, and the total weight was therefore 118.8 grams, or about 53 per cent. of that originally taken.

Methyl Acetate.—The flasks A to E contained methyl acetate with some ethyl acetate. Although special care had been taken to prevent absorption of moisture, it was found that a little water was present: in two fractionations, therefore, phosphorus pentoxide was placed in the distillation-bulb, which was heated by a water-bath. After the first fractionation the first portion of the distillate from the first fraction was taken as pure, the small residue in the still being each time rejected. There were altogether nine fractionations, and the amount of pure methyl acetate obtained was 88 grams, or about 48 per cent. of that taken. (The loss of this ester by evaporation would be greater than that of either of the other two.)

Propyl Acetate.—The flasks V to Z contained propyl acetate with some ethyl acetate. It was found that the first two residues were slightly acid, owing to hydrolysis of the esters by the trace of water present. These two residues were therefore collected separately and were shaken with a strong solution of potassium carbonate; the ester was then washed with water, dried with phosphorus pentoxide, and again distilled. Five fractionations were found sufficient to purify the propyl acetate, the residues being each time taken as pure (except the first two, which were treated as described). The total weight of pure propyl acetate was 126.8 grams, or 72 per cent. of that taken. (The loss by evaporation would be smallest in this case.)

The esters were then distilled from phosphorus pentoxide, and their specific gravities at 0° determined by Sprengel's method as modified by Perkin. The completeness of the separation was proved by the close agreement of the results with those obtained before mixing, as well as by the identity of the boiling-points with those previously determined.

The specific gravities are given below:—

Specific Gravities at 0°.

	Previous Determinations.	After Fractionation.
Methyl acetate * (a).....	·95929	·95937
„ „ (b).....	·95934	
Ethyl acetate * (a)	·92434	(1) ·92438
„ „ (b)	·92438	(2) ·92437
Propyl acetate * (a).....	·91017	·91008
„ „ (b).....	·91015	

* Two different samples of each ester had been purified and their specific gravities determined. The two results are given in each case, in order to show what error of experiment might be expected. The two samples of each ester were afterwards mixed together.

Apart from the comparison of the specific gravity of the ethyl acetate before mixing and after fractionation, a proof of the purity of this substance is afforded by the agreement between the specific gravities of the two samples, since, if the separation had been incomplete, one would have been contaminated with methyl acetate, the other with propyl acetate.

DISCUSSION.

Prof. Ramsay said the paper was a most valuable one, and would be a great aid to chemists. Distillations were usually carried out by "the rule of thumb," with the result that absolutely pure liquids could rarely be obtained.

The President inquired whether the curves representing the progress of distillation could be constructed from the very complete experiments made, and so test the assumed law.

Prof. Young thought this not possible from the numbers obtained. To test the law in this way would be very laborious.