

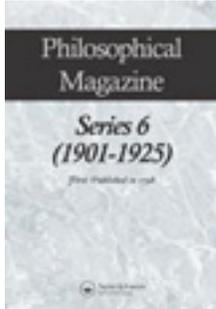
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NOVEMBER 1902.

LIX. *On the Distillation of Binary Mixtures.*
By Lord RAYLEIGH, O.M., F.R.S.*

AT various times during the past twenty years I have turned my attention to the theory of distillation, and have made experiments upon a question, as to which information seemed to be almost entirely lacking, viz., the relation between the strengths of liquid and vapour which are in equilibrium with one another when a binary mixture is subjected to distillation. In order to be intelligible I must set forth a little in detail some matters which are now fairly well known and understood, although they were not so at the time when my notes were written.

Distillation of a Pure Liquid.

The temperature of the saturated vapour just over the liquid depends upon the pressure. If the end of the condenser-tube, *e. g.*, of the Liebig type, be open, the pressure is of necessity nearly atmospheric. Suppose that in this tube a piston, moving freely, separates pure vapour from pure air. Then the whole wall of the condenser on the vapour side is almost at boiling-point. If we imagine the piston removed, the air and vapour may mix, and it is now the total pressure which is atmospheric. Wherever the temperature is below boiling there must be admixture of air sufficient to bring up the pressure.

Two or more Liquids which press independently.

This is the case of liquids like water and bisulphide of carbon whose vapour-pressures are simply added. So long

* Communicated by the Author.

as the number of ingredients remains unchanged, the composition of the vapour rising from the boiling mixture is a function of the temperature (or total pressure) only. Hence in simple distillation the composition of the distillate remains constant until perhaps one constituent of the liquid (not necessarily the most volatile) is exhausted. At this point the distillate, as well as the boiling-temperature, changes discontinuously and the altered values are preserved until a second constituent is exhausted, and so on. None of the separate distillates thus obtained would be altered by repetition of the process at the same pressure.

Liquids which form true Mixtures.

The above is as far as possible from what happens in the case of miscible liquids, *e. g.*, water and common alcohol. Here the composition of the vapour, as well as the boiling-point under given pressure, depends upon the composition of the liquid, and all three will in general change continuously as the distillation proceeds. But, so long as the total pressure is fixed, to a given composition of the liquid corresponds a definite composition of the vapour; and it is the function of experiment to determine the relation between the two. The results of such experiments may be exhibited graphically upon a square diagram (*e. g.* figs. 3 and 4, pp. 530 and 533) in the form of a curve stretching between opposite corners of the square, the abscissa of any point upon the curve representing the composition of the liquid and the ordinate representing the composition of the vapour in equilibrium with it. For the pure substances at the ends of the scale, represented by opposite corners of the square, the compositions of liquid and vapour are necessarily the same.

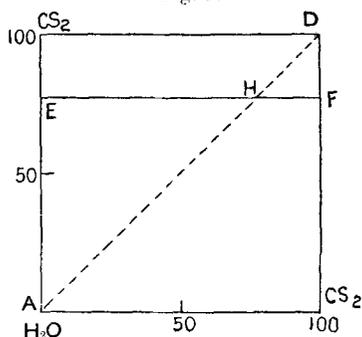
The character of the separation capable of being effected by distillation depends in great measure upon whether or not the curve meets the diagonal at any intermediate point, as well as at the extremities. If there be no such intersection, the curve lies entirely in the upper (or in the lower) triangular half of the square, so that for all mixtures the distillate is richer (or poorer) than the liquid. As the distillation of a limited quantity of mixed liquid proceeds, the composition of the residue moves always in one direction and must finally approach one or other condition of purity.

If on the other hand the curve crosses the diagonal, the point of intersection represents a state of things in which the liquid and vapour have the same composition, so that distillation ceases to produce any effect. This happens for example with a solution of hydrochloric acid at a strength of 20 per cent. (fig. 3) and with aqueous alcohol at a strength of 96 per cent. By no process of distillation can originally weak

alcohol be strengthened beyond the point named, and if (Le Bel) we start with still stronger alcohol (prepared by chemical desiccation) the effect of distillation is reversed. The vapour being now weaker (in alcohol) than the liquid, the residue in the retort *strengthens* until it reaches purity.

In the case of substances which have no tendency to mix, *e. g.*, water and bisulphide of carbon, the composition of the vapour is, as we have seen, always the same. The representative curve, reducing to a straight line parallel to the axis of abscissæ, or rather to the broken line A E F D (fig. 1),

Fig. 1.



necessarily crosses the diagonal. The point of intersection (H) represents a condition of things in which the compositions of the liquid and vapour are the same. As distillation proceeds, the residue retains its composition, and both ingredients are exhausted together.

If we commence with a liquid containing CS_2 in excess of the above proportion, the excess gradually increases until nothing but CS_2 remains behind. In the same way, if the water be originally in excess, the excess accentuates itself until the (finite) residue is pure water. The critical condition is thus in a sense unstable, and can only be realized by adjustment beforehand.

The conclusions drawn above may be generalized. Whatever may be the ingredients of a binary mixture, in the upper triangular half of the square the vapour is stronger (we will say) than the liquid, in the lower half weaker. Hence, as the liquid distills away, progress from a point in the upper half is towards diminishing abscissæ, and in the lower half towards increasing abscissæ. When, as in fig. 1, the curve in its course from A to D crosses AD from left to right, the condition represented by the point of intersection H is unstable. When, as in the case of hydrochloric acid (fig. 3), the crossing takes place from right to left, *i. e.* from the lower

half to the upper half of the square, the progress from points in the neighbourhood is always *towards* the point of intersection, so that the state represented thereby is *stable*. We may sum up by saying that if, as the liquid strengthens, the vapour having been weaker than the liquid becomes the stronger, the point of transition, representing constant distillation, is stable; but if the vapour having been at first the stronger becomes the weaker, then the point of transition is *unstable*.

The question presents itself, whether as the liquid strengthens (in a particular ingredient) the vapour necessarily strengthens with it. Does the curve on our diagram slope everywhere upwards on its course from A to D? Although a formal proof may be lacking, it would seem probable that this must be so when the ingredients mix in all proportions. A limiting case is when two ingredients do not mix at all, *e. g.*, water and bisulphide of carbon, or when the mixture divides itself into two parts of constant composition as when ether and water are associated in certain proportions. In these cases the composition of the vapour is constant for the whole or for a part of the range (Konowalow), and the representative curve is without slope.

Konowalow's Theorem.

An important connexion has been formulated by Konowalow* between the vapour-pressure, regarded as a function of the composition of the liquid with which it is in equilibrium, and the existence of a point of constant distillation. "The pressure of the vapour from a fluid consisting of two different substances is in general a function of the composition of the mixture... Let such a mixture, confined in a closed space, be maintained at a constant temperature. We may conceive this space bounded by fixed walls and by a movable piston. The conditions of stable equilibrium are then (1) that the external pressure operative upon the piston should be equal to the pressure of the saturated vapour at the given temperature; (2) that by increase, or diminution, of the vapour space the pressure should become respectively not greater, or not less, than the external pressure. In expansion the vapour-pressure can thus either remain constant, or become smaller. On the basis of this law we can establish a relation between the composition of the liquid and that of the vapour."

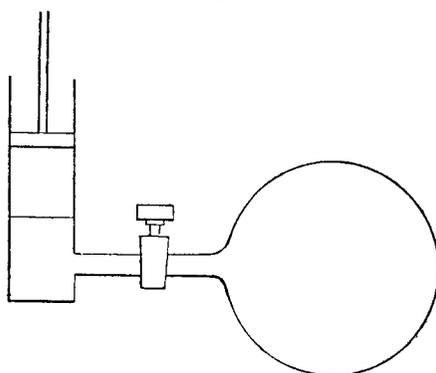
Before proceeding further I must remark that the principle, as stated, appears to need elucidation. Why should the

* Wied. *Ann.* xiv. p. 48 (1881).

equilibrium of the piston under a constant load be stable? There must of course be some position of stable equilibrium for a given load and temperature; but this might, for all that appears, correspond to complete evaporation of the liquid or to complete condensation of the vapour.

The following argument, however, suffices to show that Konowalow's principle is a necessary consequence of the second law of Thermodynamics. Suppose that the cylinder in which are contained the given liquid and vapour communicates by a lateral channel (fig. 2) with a large reservoir

Fig. 2.



filled with liquid of similar composition, and that all are maintained at the prescribed temperature. As a first operation close the tap between the vessels, and then let the piston rise a little. The motion is supposed to be so slow that equilibrium prevails throughout. The result of the expansion may be that the compositions of the liquid and of the vapour undergo a change. Now open the tap, and allow diffusion to take place, if necessary, until equilibrium is again established. On account of the large quantity of liquid in the reservoir the pressure is sensibly restored to its original value and remains undisturbed as the piston is slowly pushed back to its first position. During this cycle of operations work cannot be gained; and thus is excluded the possibility of a rise of pressure during the expansion. It follows that a fall of pressure cannot accompany compression.

Upon the basis of this principle Konowalow proceeds as follows:—Suppose that at a particular composition-ratio the pressure of vapour increases as the liquid becomes richer in a specified component. In this case the expansion of the mass cannot enrich the liquid; for if this result occurred the pressure would rise, which we have proved it cannot do.

During the expansion fresh vapour is formed ; and if the composition of the vapour were poorer than that of the liquid, the latter would inevitably be enriched by the operation. We conclude that at the point in question the vapour cannot be poorer than the liquid. In like manner if the vapour-pressure falls with increasing richness of liquid, compression of a given mass cannot enrich the liquid, and this requires that the vapour be not richer than the corresponding liquid. If we suppose the vapour-pressure to be plotted as a function of richness of corresponding liquid, we may express these results by saying that rising parts of the pressure-curve can have no representation in the lower triangle of our former diagrams (where vapour is poorer than liquid), and that falling parts cannot be represented in the upper triangle.

It is now evident that the passage from a rising to a falling part of the pressure-curve can only occur when the vapour is neither richer nor poorer than the liquid, and we arrive at Konowalow's important theorem that *any mixture, which corresponds to a maximum or minimum of vapour-pressure, has (at the temperature in question) the same composition as its vapour.*

The particular case in which one ingredient is wholly involatile is worth a moment's notice. The vapour over a solution of salt in water can never have the same composition as the liquid ; and from this we may conclude that the vapour-pressure has no maximum or minimum, or rather that there is no transition anywhere between rising and falling.

The converse of Konowalow's theorem is also not without importance. Consider two mixtures of slightly differing composition, one of which is richer than its vapour and the other poorer. Expansion of the first entails an enrichment of the liquid, and during the operation the pressure cannot rise. Expansion of the second impoverishes the liquid, and again the pressure cannot rise. The curve exhibiting pressure as a function of composition (of liquid), if it slopes at all at the two points, must slope in opposite directions. Hence by approaching nearer and nearer to the point where the compositions of vapour and liquid are the same, we see that the vapour-pressure must there be stationary in value.

An example of the use of the converse theorem is afforded by the consideration of mixtures of water and common alcohol. The question of the existence of a mixture having the same composition as its vapour is not easily settled directly, but the recent observations of Noyes and Warfel* show conclusively that the mixture containing 96 per cent.

* Am. Chem. Soc. xxiii. p. 463 (1901).

of alcohol by weight has a minimum boiling-point, and accordingly distills without change. It may be noted that the curve given by Konowalow himself would point to the contrary conclusion.

In the practical conduct of distillation it is the pressure that is constant rather than the temperature. Inasmuch, however, as pressure always rises with temperature, a maximum or minimum pressure when temperature is given necessarily corresponds with a minimum or maximum temperature when pressure is given. In the case of a solution of hydrochloric acid, for example, the thermometer marks a maximum temperature at the point where the solution distills without change.

Calculation of Residue.

Before proceeding to the experimental part of this paper it may be well to explain further the significance of the curves exhibiting the relative compositions of liquid and vapour. If w represent the whole quantity (weight) of liquid, say alcohol and water, remaining in the retort at any time, y the quantity of one ingredient (alcohol), the abscissa ξ of the curve is y/w . As the distillation proceeds for a short time w becomes $w + dw$, and y becomes $y + dy$ *; and the composition of the vapour, that is the ordinate η of the diagram, is dy/dw . Thus

$$\xi = y/w, \quad \eta = dy/dw,$$

while the functional relation between ξ and η is given by the curve, and may be analytically expressed by $\eta = f(\xi)$. Thus

$$\frac{d(w\xi)}{dw} = f(\xi),$$

whence

$$\log \frac{w}{w_0} = \int_{\xi_0}^{\xi} \frac{d\xi}{f(\xi) - \xi},$$

w_0, ξ_0 being corresponding values of w and ξ .

When ξ is small the curve is often approximately straight. If we set $f(\xi) = \kappa\xi$ we find

$$\xi/\xi_0 = (w/w_0)^{\kappa-1}.$$

For example, in the case of alcohol and water, we have for very weak mixtures $\eta = 12\xi$ approximately, so that $\kappa = 12$. As the distillation proceeds, w diminishes and ξ soon becomes exceedingly small. The halving of w implies a diminution

* dw and dy being negative.

of ξ in the ratio of $2^{11} : 1$. The residue in the retort thus approximates rapidly to pure water.

On the other hand, in the case of acetic acid and water κ is about $\frac{3}{4}$. When weak acetic acid is distilled the residue *strengthens*, but the earlier stages of the process are covered by the formula given, which now assumes the form

$$\xi / \xi_0 = (w_0 / w)^{\frac{1}{2}}.$$

In order to double the strength of the liquid remaining in the retort, 15/16 of it would have to be distilled away, or again, in order to increase the strength in the ratio of 3 : 2, the distillation must proceed until the liquid is reduced in the ratio of 16 : 81, or nearly of 1 : 5. An experiment of this sort upon acetic acid is recorded below.

Observations.

The experimental results about to be given were obtained by simple distillation of mixtures of known composition. In order to avoid too rapid a change of composition, somewhat large quantities were charged into a retort and were kept in vigorous ebullition. By special jacketing arrangements security was taken that the upper part of the retort should be maintained at a distinctly higher temperature than the liquid, so that there could be no premature condensation which would vitiate the result. *All* the vapour rising from the liquid must be condensed in the specially provided Liebig condenser and be collected as distillate. Subject to this condition, and in view of the rapid stirring effected by the rising vapour, it would seem safe to assume that the distillate really represents the vapour which is in equilibrium with the liquid at the time in question. The compositions of the liquid and vapour are of course continually changing as the distillation proceeds.

The distillates (including the first drop) were collected in 50 c.c. measuring flasks. It will save circumlocution to speak of a particular case, and I will take that of alcohol and water, for which the analyses were made by specific gravity. The successive collections of 50 c.c. show an increasing specific gravity corresponding to a diminishing strength. The specific gravity of each gives the total weight, and the strength, deduced from tables, allows us to calculate the alcohol and water in each collection. The total alcohol and water originally present in the retort being known in the same way, we are able to deduce by subtraction the quantities remaining in the retort at each stage, and thus to compare the strengths of corresponding liquid and vapour. In the

reduction any particular distillate is considered to correspond with the mean condition of the liquid before and after its separation therefrom.

If the process above sketched could be absolutely relied on, it would be possible, starting with a strong spirit in the retort, to obtain from one distillation data relating to a great variety of strengths. But this method is not to be recommended, as the errors would tend to accumulate. The first 50 c.c., condensed under somewhat abnormal conditions, was not used directly, but only to allow for the change going on in the retort. The 2nd, 3rd, and 4th collections were usually calculated so as to show the strengths of these distillates in comparison with that of the liquid, but they were regarded rather as checks upon one another than as independent results relating to an altered state of affairs.

Alcohol and Water.

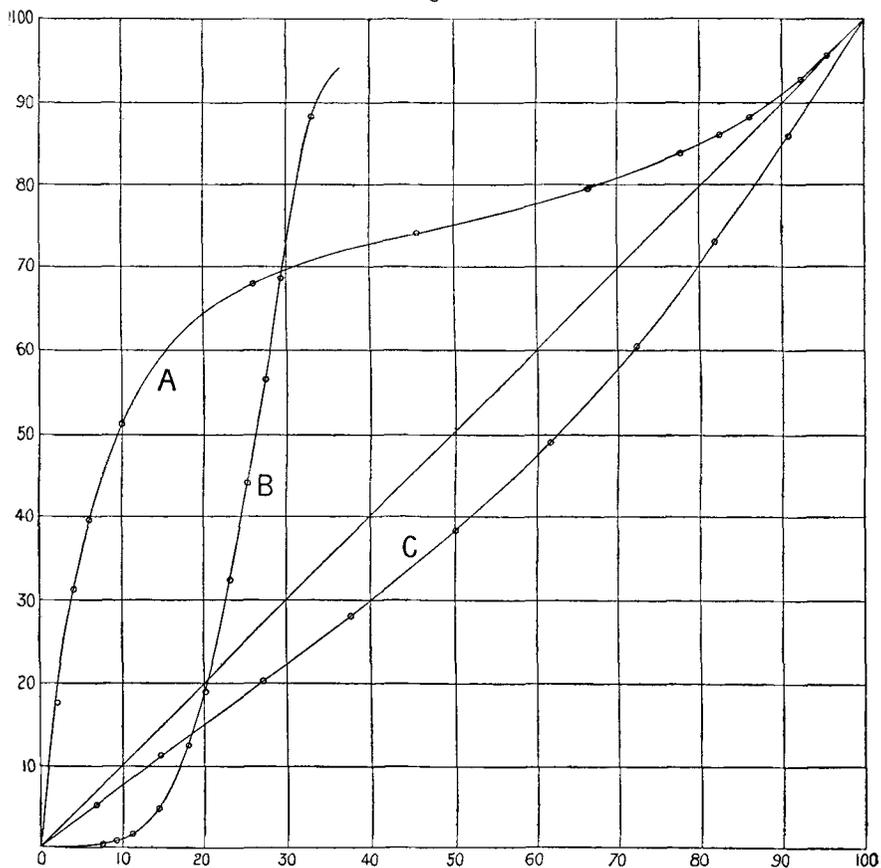
Observations upon mixtures of water and ethyl alcohol, sufficient to give a nearly complete curve, were made in 1891 and again in 1898 with good general agreement. The specific gravities were found in the balance with a bottle of 20 c.c. capacity, and the calculations of strength were by Mendeleef's tables with appropriate temperature correction. The results of the second series are given in the accompanying table and are exhibited as a curve, A, in fig. 3. The strengths are throughout reckoned by weight.

Date 1898.	Strength of Liquid.	Strength of Vapour.
May 4	·01970	·1750
„ 3	·03982	·3159
„ 5	·0601	·3979
„ 9	·0988	·5145
„ 10	·2586	·6803
„ 13	·4562	·7412
„ 16	·6606	·7976
„ 17	·7739	·8414
„ 20	·8221	·8622
„ 23	·8594	·8849
„ 24	·9241	·9284
„ 25	·9555	·9545

The observation of May 4 thus signifies that to a liquid containing by weight 1·97 per cent. of alcohol there corresponds a vapour containing by weight 17·5 per cent. of alcohol. From the results of May 24 we see that when the liquid reaches 92 per cent. the vapour is but little the stronger,

and the difference practically disappears at 95 per cent. Indeed according to May 25 the vapour is a little the

Fig. 3.



A. Alcohol and Water. B. Hydrochloric Acid and Water. C. Acetic Acid and Water.

weaker at this point. The difference, however, is not to be trusted, since the difficulties of manipulation, depending partly upon the attraction of strong alcohol for aqueous vapour, are much increased at this stage. It was these difficulties and the uncertainty as to what exactly happened with spirit stronger than 95 per cent. that retarded the publication of the work. I had intended to make further experiments upon this point, but the matter was postponed from time to time. The observations of Noyes and Warfel (*l. c.*)

seem now to remove all doubt. The existence of a minimum boiling-temperature for a strength of 96 per cent. shows that the curve there crosses the diagonal. Between this point and 100 per cent. the vapour is the weaker, and the curve lies in the lower triangular half of the square. But the deviation from the diagonal in this region is probably extremely small.

The following from Noyes and Warfel's table may be useful:—

Strength.	Boiling-point.	Strength.	Boiling-point.
100	78°300	85	78°645
99	78°243	80	79°050
98	78°205	75	79°505
97	78°181	65	80°438
96	78°174	55	81°77
95	78°177	48	82°43
94	78°195	35	83°87
93	78°227	26	85°41
92	78°259	20	87°32
91	78°270	10	91°80
90	78°323	0	100°00

Hydrochloric Acid and Water.

One of the ingredients of the mixture being gaseous under ordinary conditions, the observations are limited to that portion of the curve for which the strength of the liquid does not exceed 35 per cent., unless freezing appliances are called into play. No attempt was made in the present experiments to pass the above limit, the object being merely to determine with moderate accuracy that part of the curve with which we are usually concerned in the laboratory. It was known from the experiments of Roscoe and others that the curve would cross the diagonal at the strength of about 20 per cent.

The general plan of the work was the same as in the case of alcohol and water, but the strengths were usually determined chemically. In the case of the stronger acids it was not possible to condense the vapour at atmospheric temperature; and I contented myself with a calculation in which the strength of the vapour was inferred from observations of the quantity and strength of the liquid in the retort before and after the operation. Results obtained in this way are doubtless of minor accuracy.

It may be worth while to reproduce in tabular form the data relating to the weakest acid.

Distillation of Hydrochloric Acid.—Sept. 13, 1898.

No.	Volume in c.c.	Specific gravity.	Total weight.	Per-centage of HCl.	Weight of HCl.	Weight of H ₂ O.	HCl remaining in re-tort.	H ₂ O remaining in re-tort.	Total remain-ing.	Per-centage of HCl remain-ing.
0	1800	1·031	1855·8	6·0	111·4	1744·4	6·0
1	250	1·0013	250·32	0·26	0·65	249·7	110·7	1494·7	1605·4	6·9
2	250	1·0023	250·58	0·45	1·12	249·4	109·6	1245·3	1354·9	8·1
3	250	1·0038	250·95	0·76	1·90	249·0	107·7	996·3	1103·9	9·8
4	250	1·0076	251·90	1·53	3·86	248·0	104·0	748·3	852·3	12·2

The first column contains the numbers of the successive distillates from 1 to 4, the entry 0 referring to the mixture with which the retort was originally charged. The volume of this mixture was 1800 c.c. of specific gravity 1·031 and of 6·0 per cent. strength. Of the total weight 1855·8 gms., 111·4 gms. is hydrochloric acid and 1744·4 gms. water. In like manner the volume of the first distillate is 250 c.c., the specific gravity 1·0013, the total weight 250·32 gms., of which 0·65 gms. is HCl and 249·7 gms. H₂O. The residue in the retort after the first 250 c.c. has been distilled over is accordingly composed of 111·4—0·65 or 110·7 gms. HCl and 1744·4—249·7 or 1494·7 gms. H₂O, making 1605·4 gms. in all. At this stage the percentage strength of the liquid remaining in the retort is 6·9. The strengths of the liquid in the retort after the 1st, 2nd, . . . 4th distillates have been removed are found in this way to be 6·9, 8·1, 9·8, and 12·2 per cent. The first distillate, whose strength is 0·26 per cent., thus corresponds with a liquid whose strength varied from 6·0 to 6·9 per cent., on an average 6·45 per cent. We thus obtain the following corresponding strengths:—

Percentage Strengths.	
Liquid.	Vapour.
6·45	0·26
7·50	0·45
8·95	0·76
11·00	1·53

It is hardly worth while to record all the separate results. In addition to the above the following will suffice for the construction of the curve. In the three last the strengths of

the distillates were not directly observed, but were calculated from the condition of the liquid before and after as already mentioned.

Percentage Strengths.

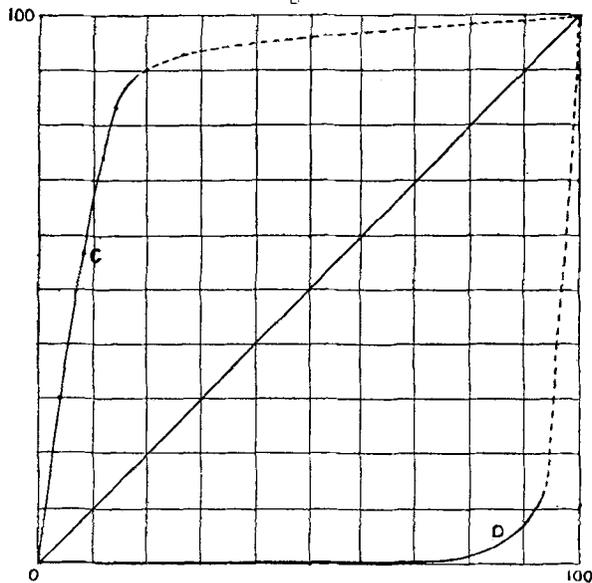
Date (1898).	Liquid.	Vapour.
Sept. 21	14.5	4.46
" 28	18.0	12.8
Oct. 10	20.3	18.9
" 12	23.3	32.4
" 14	25.2	44.2
" 15	27.4	56.6
" 18	29.0	68.8
" 19	32.8	88.3

The results are plotted in Curve B, fig. 3.

Ammonia and Water.

In this case the analysis was by specific gravity and the results were somewhat rough, the intention being merely to obtain an approximation to the form of the curve. On this account they are plotted upon a smaller scale C, fig. 4, the

Fig. 4.



C. Ammonia and Water. D. Sulphuric Acid and Water.

dotted portion of the curve being conjecturally added to indicate the progress towards the corner of the square.

Lord Rayleigh on the
Sulphuric Acid and Water.

The distillates were here determined chemically. From acid in the retort of less strength than 60 per cent. the distillate failed to redden litmus. From 75 per cent. acid the distillate contained about one-thousandth part of H_2SO_4 . From 81 per cent. the distillate contained 1·6 per cent. ; from 90 per cent. the distillate contained 7·1 per cent. ; and from 93 per cent. liquid the distillate contained 12·8 per cent. of acid. The curve is given in D, fig. 4, the dotted portion for strengths of liquid greater than 93 per cent. being conjectural.

Acetic Acid and Water.

This case was examined as likely to exemplify a very different behaviour from any of the others, since it was known that these substances are not easily separated by distillation. The retort was charged with 1000 c.c. of mixture and two distillates were collected of 150 c.c. each. The analyses were conducted chemically and the results calculated as already explained. Thus the first distillate was considered to correspond with the mean strength in the retort before and after its separation. The following were the results obtained :—

Acetic Acid and Water.

Date 1902.	Strength of Liquid.	Strength of Vapour.
Aug. 18	·0677	·0510
Aug. 11	·1458	·1136
Aug. 6	·2682	·2035
Aug. 18	·3746	·2810
Aug. 5	·4998	·3849
Aug. 23	·6156	·4907
Aug. 22	·7227	·6045
Aug. 21	·8166	·7306
Aug. 20	·9070	·8622

It appears that the vapour is always weaker than the liquid, but that the difference is never great. A plot of the corresponding strengths is given in C (fig. 3, p. 530).

In illustration of the preceding theory an experiment was tried in which three-quarters of the original volume of liquid was distilled over. The original liquid consisted of 1000 c. c. of acid of density 1·010, and of strength (as determined chemically) ·0757, representing as usual the proportion of the weight of acetic acid to the whole weight. The residue

measuring 250 c. c. was of density 1.016 and of strength .1100. From these data we find

$$\log (\xi / \xi_0) = 1624, \quad \log (w_0 / w) = .5995,$$

whence

$$1 - \kappa = .27, \quad \kappa = .73.$$

The number denoted by κ represents the ratio of strengths of vapour and liquid when weak mixtures are distilled.

A new Apparatus with uniform Régime.

In the theory and experiments so far considered the distillation has always been supposed to be simple, that is, the vapour rising from the boiling liquid is supposed to be removed and to be condensed as a whole, so that the distillate has the same composition as the vapour leaving the boiling liquid. In practice, as is well known, this condition is often and advantageously violated. A preliminary partial condensation of the vapour in the still-head frees it from some of the less volatile ingredient; and, when the residue is condensed and collected, the more volatile ingredient is obtained in a nearer approach to purity. Prof. S. Young has shown that the principle is more effectively carried out if the still-head be maintained at a suitable temperature.

Even with a preliminary partial condensation in the still-head, the "fractionation" of a mixture is usually regarded as a very tedious operation. The stock of mixture in the retort is constantly changing its composition as the distillation and partial condensation proceed, and no uniform *régime* can be established. Although theoretical simplicity and practical convenience are not always conjoined, a uniform *régime* seems very desirable, and it excludes the usual arrangement in which the whole supply of mixture is charged into the retort. The return into the retort of the liquid first condensed from the original vapour is also objectionable.

The problem of distillation may be stated to be the separation from a binary mixture of the whole of the two components in, as nearly as may be, a state of purity. There is no theoretical reason why this should not be effected at one operation; but for this purpose the mixture must be fed in continuously and not at the place of highest or lowest temperature. A description of the procedure followed in some illustrative experiments will make the nature of the process plain.

The mixtures actually employed were of water and common alcohol. The choice was perhaps not a happy one, as in consequence of the peculiar properties of strong alcohol it

was unlikely that a distillate could be obtained stronger than about 90 per cent. As regards apparatus, the retort and still-head are replaced by a long length (12 metres) of copper tubing, 15 mm. in diameter. This is divided into two parts, arranged in spirals, like the worms of common condensers, and mounted in separate iron pails. The lower and longer spiral was surrounded with water which was kept boiling. The water surrounding the upper spiral was maintained at a suitable temperature, usually 77°C . The copper tubes forming the two spirals were connected by a straight length of glass, or brass, tubing of somewhat greater bore, and provided with a lateral junction through which the material could be supplied. The connecting piece and the spirals were so arranged that the entire length was on a slight and nearly uniform gradient, rising from near the bottom of the lower pail to the top of the upper pail. On leaving the latter the tube turned downwards and was connected with an ordinary Liebig's condenser capable of condensing the whole of the vapour which entered it. At the lower end of the system of tubing the watery constituent is collected. In strictness the receiver should be connected air-tight and be maintained at 100° . In distilling the stronger mixtures (60 or 75 per cent. alcohol) this precaution was found advisable or necessary; but in the case of the weaker ones the water could be allowed to discharge itself through a short length of pipe whose end was either exposed to the atmosphere or slightly sealed by the liquid in the receiver.

The feed of the mixture was arranged as a visible and rather rapid succession of drops, and was maintained at a uniform rate. In the case of the stronger mixtures the evaporating power of the lower coil was hardly sufficient, and was assisted by applying heat to the feed, so that a good proportion was evaporated before reaching the main tube. The weaker mixtures on the other hand could be fed in without any preliminary heating. The uniform *régime* should be maintained long enough to ensure that the liquids collected at the two ends shall be fairly representative and not complicated by anything special that may happen before the uniform *régime* is established.

During the operation every part of the tube (not too near the ends) is occupied by a double stream—an ascending stream of vapour and a descending stream of liquid. Between these streams an exchange of material is constantly taking place, the liquid, as it descends, becoming more aqueous and the vapour, as it rises, becoming more alcoholic. In view of the slowness of the feed and the length of the

tube, we may regard the liquid and the vapour as being everywhere in approximate equilibrium. At the lower end, since the pressure is atmospheric and the temperature scarcely below 100° , there can be little alcohol; for similar reasons at the upper end there cannot be much water, although the exclusion is here less complete on account of the peculiar character of the curve representing the relation of compositions at this extreme.

Experiments were tried with four different strengths of mixture—20, 40, 60, and 75 per cent. of alcohol. In all cases the water was collected nearly pure, never containing more than $\frac{1}{2}$ per cent. of alcohol. The alcoholic part condensed from the upper end varied but little. The weakest (from the 20 per cent. mixture) was of 89 per cent., and the strongest was of 90.3 per cent. All strengths are given by *weight*, and were calculated by Mendeleef's tables from the observed specific gravities with suitable temperature correction. The watery constituent which, not having been evaporated, sometimes looked a little dirty, was usually redistilled so as to obviate any risk of its purity being overestimated. In some cases it could not be distinguished from pure water.

The apparatus illustrates very well the principles of ideal distillation, and its performance may be regarded as satisfactory. When once the conditions, as to preliminary heating (if necessary) and as to rate of feed, have been found for a particular mixture, the continued working is almost self-acting, or at any rate could be made so without much difficulty; and it is probable that separations, otherwise very troublesome, could be easily effected by use of it.

LX. *Change of the Modulus of Rigidity of Ferromagnetic Substances by Magnetization.* By K. HONDA, *Rigakushi*, S. SHIMIZU, *Rigakushi*, and S. KUSAKABE, *Rigakushi*.*

1. **WE** have already seen that the change of elasticity by magnetization is not so small as generally admitted. The present experiments deal with the change of rigidity by magnetization. The investigation is especially important inasmuch as the change of rigidity is reciprocally related to that of magnetization by torsion.

In the course of his experiments on the mutual relations between torsion and magnetization, G. Wiedemann† observed

* Communicated by Prof. Nagaoka.

† Wiedemann's *Electricität*, iii. p. 796.