LXXIII.—*The Preparation of Absolute Alcohol from Strong Spirit.*

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OWING to the fact that ethyl alcohol, like *n*-propyl, *iso*propyl, and *tert.*-butyl alcohols, although miscible with water in all proportions, forms with it a mixture of constant boiling point which distils without change of composition at a temperature lower than either component, it is impossible by any process of fractional distillation to separate the pure alcohol from a dilute solution. All that can be done is to separate the mixture of constant boiling point on the one hand, and water on the other, from the solution. In the case of the other alcohols referred to, if we remove a portion of the water from the mixture of constant boiling point by some other method, then by fractional distillation of the stronger alcohol with a very efficient still-head we can effect its separation into the pure alcohol and the mixture of constant boiling point.

Pure ethyl alcohol, however, boils less than 0·2° higher than the mixture of minimum boiling point, and such a separation is therefore impracticable.

The method which has invariably been employed to prepare absolute alcohol is to treat the strongest spirit obtainable by distillation with a dehydrating agent, and the action of such agents has been studied by many investigators, notably by Mendeléeff and by Squibb.

In his classical paper on this subject, Mendeléeff (*Ann. Phys. Chem.*, 1869, [ii], **138**, 230) discusses the behaviour of different dehydrating agents and concludes that freshly ignited lime is the only substance capable of giving good results, and that even when lime is employed special precautions must be taken.

The results obtained by Mendeléeff with four different specimens show excellent agreement, the greatest difference from the mean sp. gr. at 0°/4°, 0·806254, being only 0·000011, but Mendeléeff himself states that when the alcohol was freshly distilled over lime he noticed an ethereal odour which, however, disappeared on repeated distillation, although the sp. gr. remained unchanged. The value 0·80625 has been almost universally adopted as the correct sp. gr. at 0°/4°, but Squibb (*J. Amer. Chem. Soc.*, 1893, **15**, 126) has obtained even lower values by slow percolation through lime. In an earlier investigation, Squibb had found the sp. gr. 0·79350 at 15·6°/15·6°, which corresponds to 0·80581 at 0°/4°, but in the paper referred to he states that after long contact with lime and subsequent percolation many times through an improved apparatus, alcohol was obtained with a somewhat higher

specific gravity.   The results were not perfectly concordant, the mean of the best being given as 0·793562 at 15·6°/15·6°, corresponding to 0·80587 at 0°/4°.   Squibb states that in his opinion absolute alcohol had not yet been obtained.

When two liquids of different chemical type are distilled together, a definite mixture of minimum boiling point in many cases distils over first, the last portion of the distillate consisting of that component which was originally present in excess.   Ethyl alcohol may be regarded as a derivative of water and as belonging to the water type $H \cdot O \cdot C_2H_5$, or as a derivative of ethane, or, more generally, of a paraffin, $C_2H_5 \cdot OH$. In its properties, it exhibits analogies in some respects to water and in others to the paraffins.   Most dehydrating agents which react or combine with water behave in a somewhat similar manner towards the alcohols, though to a less degree, and to a diminishing extent as the molecular weight increases, and this accounts for the unsatisfactory results obtained with them.   Thus phosphoric oxide gives phosphoric acid with water, and a mixture of ethyl hydrogen phosphates with ethyl alcohol; with barium oxide, water forms barium hydroxide, whilst ethyl alcohol forms, according to Forcrand, a compound $3BaO,4C_2H_6O$; sodium acts in precisely the same way on the alcohols as on water, but the intensity of the action diminishes rapidly as the complexity of the alkyl group increases ; calcium chloride forms a crystalline hexahydrate with water, and a crystalline tetra-alcoholate with methyl or ethyl alcohol ; the behaviour of anhydrous copper sulphate is striking ; it dissolves rapidly in water, and, on evaporation, crystals of $CuSO_4,5H_2O$ are deposited ; in methyl alcohol, it dissolves slowly, but to a considerable extent, giving a blue solution from which, according to Forcrand, greenish-blue crystals of $CuSO_4,CH_4O$ may be obtained ; anhydrous copper sulphate is, however, quite insoluble in ethyl alcohol, and will extract some water from strong spirit, but it is not a sufficiently powerful dehydrating agent to remove the whole.

If we compare the homologous normal primary alcohols together, we find that in other respects also, as the molecular weight rises, the alkyl group has increasing, and the hydroxyl group diminishing, influence, and that the properties recede from those of water and approach those of the corresponding paraffin.   The table of boiling points on p. 709 shows this clearly.

Thus methyl alcohol boils only 35·3° lower than water, but 228·7° higher than methane, whilst cetyl alcohol boils 244° higher than water, but only 56·5° higher than the corresponding paraffin.   Again, whilst methyl, ethyl, and propyl alcohols are miscible in all proportions with water, butyl alcohol is only partially miscible, and cetyl alcohol is practically non-miscible with water.

Lastly, while a mixture of methyl alcohol and water distils normally,

Number of carbon atoms.	Boiling points.				
	Paraffin.	Δ.	Alcohol.	Δ.	Water.
1	$-164°$	$+228\cdot7°$	$+64\cdot7°$	$-35\cdot3°$	$100°$
2	-93	$171\cdot3$	$78\cdot3$	$-21\cdot7$	—
3	-45	$142\cdot4$	$97\cdot4$	$-2\cdot6$	—
4	$+1$	$116\cdot0$	$117\cdot0$	$+17\cdot0$	—
5	$36\cdot3$	$101\cdot7$	$138\cdot0$	$38\cdot0$	—
6	$69\cdot0$	$88\cdot0$	$157\cdot0$	$57\cdot0$	—
7	$98\cdot4$	$77\cdot6$	$176\cdot0$	$76\cdot0$	—
8	$125\cdot6$	$70\cdot4$	$196\cdot0$	$96\cdot0$	—
16	$287\cdot5$	$56\cdot5$	$344\cdot0$	$244\cdot0$	—

both components being easily separated, ethyl and propyl alcohols form, with water, mixtures of minimum boiling point, and the behaviour of butyl alcohol and water approaches that of two non-miscible liquids.

We cannot well study the miscibility of the alcohols with the corresponding paraffins, because the first four are gaseous at the ordinary temperature and most of them are difficult to prepare in a pure state. Normal hexane, however, can be obtained without much difficulty, and we find that, although the lowest alcohols are miscible with this hydrocarbon in all proportions, they form with it mixtures of minimum boiling point. Benzene is much more easily obtained than hexane, and behaves in a similar manner. The behaviour of mixtures of benzene with the lower alcohols has been studied by Miss Fortey and myself, and is fully considered in a separate paper; it will be sufficient here to state that whilst methyl, ethyl, *iso*propyl, *n*-propyl, *tert*.butyl, and *iso*butyl alcohols form mixtures of minimum boiling point with benzene, *iso*amyl alcohol does not.

Thus ethyl alcohol forms mixtures of minimum boiling point, both with water and with benzene (or hexane), whilst benzene and water are practically non-miscible and distil over together at a temperature lower than the boiling point of either pure liquid; it seemed reasonable to expect that a particular mixture of all three liquids would boil constantly at a still lower temperature. The original mixture would, in that case, tend to separate on distillation into three instead of two fractions :—(1) a definite mixture of all three liquids boiling at a lower temperature than any of the three components, or than any mixture of any two of them; (2) a mixture of two components boiling at a lower temperature than any single one; (3) that component which was originally in excess.

When aqueous alcohol is distilled with a dehydrating agent, the water is more or less completely retained in the still, the dried alcohol passing over as the distillate; if, however, a mixture of ethyl alcohol,

benzene, and water behave as suggested above, it should be possible to reverse the process, the water being carried over in the first part of the distillate and pure alcohol coming over last. Such a method would be advantageous for this reason, among others, that it is almost always easier to separate the least volatile component of a mixture in a pure state by distillation than the more volatile components. These anticipations were fulfilled, and it was, in fact, found possible to eliminate the water from strong spirit by distillation with benzene.

In all the experiments carried out in connection with this investigation, I have had the advantage of the able co-operation of Miss E. C. Fortey, B.Sc.

The following table gives the boiling points of ethyl alcohol, benzene, and water, and of the mixtures of constant boiling point that they can form, also the composition of these mixtures.

The benzene-water values were calculated from the known vapour pressures of benzene and water, these two liquids being practically non-miscible, and their correctness was confirmed by actual experiments ; the other values were determined experimentally :

Liquid of constant boiling point.	Boiling point.	Percentage composition.		
		Alcohol.	Water.	Benzene.
1. Alcohol, water, and benzene (W.A.B.)...	$64\cdot85°$	$18\cdot5$	$7\cdot4$	$74\cdot1$
2. Alcohol and benzene ...(A.B.)...	$68\cdot25$	$32\cdot41$	—	$67\cdot59$
3. Water and benzene ......(W.B.)	$69\cdot25$	—	$8\cdot83$	$91\cdot17$
4. Alcohol and water ......(A.W.)...	$78\cdot15$	$95\cdot57$	$4\cdot43$	—
5. Alcohol ....(A.)...	$78\cdot3$	100	—	—
6. Benzene ....(B.)...	$80\cdot2$	—	—	100
7. Water ....(W.) .	$100\cdot0$	—	100	—

It will be seen that the lowest boiling point is that of the ternary mixture (W.A.B.), so that whatever mixture of the three liquids is distilled—unless one constituent is present in relatively very small quantity —this ternary mixture will come over first. If there is more than sufficient benzene to carry over the whole of the water, and if the alcohol is present in excess, the ternary mixture will be followed by the binary (A.B.) mixture, and the last substance to come over will be alcohol. This is the case, for instance, if we distil a mixture of equal weights of benzene and, say, 93 per cent. (by weight) alcohol with a very efficient still-head. The distillate is at first turbid, and on standing separates into two layers, although the original mixture is quite clear ; the temperature remains constant at $64\cdot85°$ for a long time, it then rises slowly, but with increasing rapidity, to the middle

temperature, 66·55°, between 64·85° and 68·25°, when the distillate ceases to be turbid; the temperature then rises more and more slowly, and becomes nearly steady for some time at or a little below 68·25°, when the binary (A.B.) mixture comes over. Then the temperature rises again with increasing rapidity, and very rapidly indeed as it passes the middle temperature, 73·3°, between 68·25° and 78·3°; afterwards, the rise becomes slower and slower until the boiling point of alcohol is reached.

It should thus be theoretically possible to carry over the whole of the water in the first fraction and to remove the whole of the remaining benzene in the second, leaving pure alcohol in the last. It will, however, be noticed that the difference between the boiling points of the ternary (W.A.B.) mixture and the binary (A.B.) mixture is only 3·4°, so that the separation is a difficult one and in practice it was found that even when the mixture was distilled through an 18 column Young and Thomas dephlegmator at the rate of 1 drop per second, the alcohol in the final distillate, though containing the merest trace of benzene, still retained about 1·4 per cent. of water as compared with 7·4 per cent. in the original alcohol.

By redistilling the partially dehydrated alcohol once or twice with a further quantity of benzene, the water could, however, be finally eliminated.

It is convenient to collect the distillate in four fractions :—

I. From 64·85° to about 67·5°. This consists mainly of the ternary (W.A.B.) mixture.

II. From 67·5° to about 73°. This consists chiefly of the binary (A.B.) mixture.

III. From about 73° to 78·3°. The distillate should be collected in III for a little time after the temperature has become constant at 78·3° to remove the benzene as completely as possible. This fraction is much richer in alcohol than II; it should be relatively very small in amount.

IV. The dehydrated alcohol; it is not essential that this should be distilled, it may simply be run off from the still.

Fraction I, boiling at 64·85° *to about* 67·5°.

This distillate is turbid and separates into two layers, the smaller (and usually but not necessarily the lower) layer consisting of water, a good deal of alcohol, and some benzene, the larger layer consisting of benzene with a good deal of alcohol and a little water. On adding more water, shaking, and allowing to stand, two layers are again formed; the lower one, A, contains most of the alcohol and water with very little benzene; the upper one, B, contains nearly all the benzene

3 B 2

with very little alcohol and water. The two layers should now be separated and the benzene washed once or twice with water to remove the alcohol (and also the water, since alcoholic benzene dissolves more water than pure benzene) more completely ; the water may be added to A.

The two liquids, A and B, should now be distilled, preferably with an efficient still-head.

Distillation of A.—On distillation, this liquid tends to separate into three fractions : (1) a very small quantity of the ternary (W.A.B.) mixture boiling at $64\cdot85°$; (2) the binary (A.W.) mixture boiling at $78\cdot15°$; (3) water. The whole of the benzene comes over below $78\cdot15°$, and this small fraction may be added to other quantities of the ternary mixture. The rest of the distillation consists simply in the recovery of strong spirit from dilute alcohol.

Distillation of B.—On distillation, B tends to separate into three fractions : (1) a minute quantity of the ternary mixture, but this may be absent if the benzene has been very thoroughly washed with water ; (2) the binary (W.B.) or possibly (A.B.) mixture, also; exceedingly small in amount ; (3) pure benzene.

There is no advantage in keeping the two first fractions separate, they may be collected together and added to the ternary mixture from other distillations. After the temperature has reached $80\cdot2°$, the liquid in the still consists of pure benzene and there is no necessity to distil it.

Fraction II, boiling from about $67\cdot5°$ to about $73°$.

This distillate is clear and consists chiefly of the binary (A.B.) mixture, but it contains a little water. Dilute alcohol and benzene might be obtained from it by addition of water, but it is more advantageous to add it to the next mixture of strong spirit and benzene that is to be distilled. If equal weights of strong spirit and benzene are again taken and the (A.B.) mixture is added, the alcohol obtained will be drier and the quantity a little larger. The fractions obtained in this case will be the same as before, but fraction II (b. p. $67\cdot5—73°$) will be larger. If at any time the quantity becomes too large to be made use of in this way, water may be added to a portion and pure benzene and strong spirit recovered as described under I.

Fraction III, boiling at about $73°$ to $78\cdot3°$.

This fraction should be relatively small ; it consists chiefly of alcohol with some benzene and very little water. It is not worth while to redistil the fraction from a single operation, but the fractions from a series of distillations should be added together and stored until the quantity is large enough to be redistilled.

On distillation, fraction (1) will be absent or very small ; fraction (2) will be fairly large ; fraction (3) about the usual small quantity ; fraction (4) large. Thus an additional quantity of partially dehydrated alcohol will be obtained.

Fraction IV, boiling at $78 \cdot 3°$.

This fraction consists of alcohol containing no more than a trace of benzene and nearly free from water. It is impossible to state definitely what percentage of water will remain in the alcohol ; the more efficient the still-head, the slower the distillation and the larger the amount of benzene originally added, the drier will the alcohol be.

In this process, the whole of the dehydrating agent, benzene, is recovered except the small amount lost by evaporation.   There need also be hardly any loss of alcohol.   As there is no chemical reaction, there is no possibility of introducing any impurity into the alcohol except, perhaps, a minute trace of benzene.

A considerable number of distillations with an 18 column Young and Thomas dephlegmator were carried out by this method at the rate of 1 drop per second.   The alcohol employed was obtained from Kahlbaum ; its sp. gr. at $0°/4°$ was $0 \cdot 82907$, and it therefore contained $7 \cdot 4$ per cent. of water by weight ; it was quite free from other impurities.

After the temperature had reached $78 \cdot 3°$, the residual alcohol was collected in fractions and the sp. gr. of the first and last were, as a rule, determined.   The results obtained were as follows :

(i) A mixture of 325 grams of $92 \cdot 6$ per cent. alcohol (sp. gr. $0 \cdot 82907$) and 325 grams of benzene (dried with sodium) was distilled.   After the temperature had reached $78 \cdot 3°$, the following fractions were collected :

	Weight.	Sp. gr. at $0°/4°$.	Percentage of water by weight from Mendeléeff's data.
1............	$20 \cdot 9$ grams.	$0 \cdot 81176$	$1 \cdot 85$
2............	$85 \cdot 6$,,	—	—
3............	$35 \cdot 7$,,	$0 \cdot 80976$	$1 \cdot 10$
Residue ...	$22 \cdot 8$,,	—	—
	$165 \cdot 0$,,		

It is very probable that the first fraction was in this case collected a little too soon, and contained a perceptible amount of benzene, which would raise its sp. gr.

(ii) Similar to the first, but the benzene was added in three portions. The weight of each liquid was 200 grams, and that of the dehydrated alcohol $89 \cdot 5$ grams.   The sp. gr. of the first and last fractions

were 0·81043 and 0·80946, corresponding to 1·40 and 1·03 per cent. of water respectively.

(iii) A mixture of 254 grams of alcohol of sp. gr. 0·81033 (water 1·37 per cent.) was distilled with 169 grams of benzene. At 78·3°, the results were as follows :

	Weight.	Sp. gr. at 0°/4°.	Water per cent.
1............	27·8 grams.	0·80741	0·38
2.............	48·3 ,,	—	—
3............	56·6 ,,	0·80683	0·13
Residue ...	11·5 ,,	—	—
	144·2 ,,		

(iv) The mixture distilled consisted of 282 grams of 92·6 per cent. alcohol, 282 grams of benzene, and 270 grams of binary (A.B.) mixture from previous distillations :

	Weight.	Sp. gr. at 0°/4°.	Water per cent.
1............	23·6 grams.	—	—
2............	33·6 ,,	0·80822	0·62
Residue ...	108·7 ,,	—	—
	165·9 ,,		

(v) To 275 grams of 92·6 per cent. alcohol and 275 grams of benzene, 379 grams of a previous distillate collected between 66·5° and 78·3° was added :

	Weight.	Sp. gr. at 0°/4°.	Water per cent.
1............	18·6 grams.	—	—
2.............	23·7 ,,	0·80789	0·50
Residue ...	121·3 ,,	—	—
	163·6 ,,		

(vi) The 92·6 per cent. alcohol was first redistilled to remove a little water. A mixture of 275 grams of redistilled alcohol, 275 grams of benzene, and 254 grams of the fraction collected from the previous distillation between 67·35° and 78·3° was distilled :

	Weight.	Sp. gr. at 0°/4°.	Water per cent.
1............	17·3 grams.	—	—
2............	22·0 ,,	0·80761	0·47
Residue ...	132·0 ,,	—	—
	171·3 ,,		

(vii) The mixture distilled consisted of 289 grams of alcohol, con-

taining a little more than 0·3 per cent. of water and 192 grams of benzene :

	Weight.	Sp. gr. at 0°/4°.	Water per cent.
1............	12·4 grams.	—	—
2............	24·2 ,,	0·80660	about 0·1
3............	67·1 ,,	—	—
4............	53·0 ,,	0·80638	trace
Residue ...	15·0 ,,	—	—
	171·7 ,,		

(viii) A mixture consisting of 99·6 per cent. alcohol, (A.B.) fractions from previous distillations, and benzene, the whole estimated to contain 370 grams of alcohol and 310 grams of benzene, was distilled :

	Weight.	Sp. gr. at 0°/4°.	Water per cent.
1............	20·8 grams.	—	—
2............	22·9 ,,	0·80673	about 0·11
3............	94·4 ,,	—	—
4............	24·9 ,,	0·80634	dry
Residue ...	39·0 ,,	—	—
	202·0		

(ix) The whole of the driest alcohol, 371·5 grams, was distilled with 249 grams of benzene :

	Weight.	Sp. gr. at 0°/4°.
1.................	26·4 grams.	0·80645
2.................	102·3 ,,	—
3.................	29·5 ,,	0·80636
Residue	25·3 ,,	—
	183·5	

(x) The alcohol from the last distillation, 182·3 grams, was distilled with 90 grams of benzene :

	Weight.	Sp. gr. at 0°/4°.
1.................	24·6 grams.	0·80644
2.................	20·4 ,,	—
3.................	36·0 ,,	0·80634
Residue	14·0 ,,	—
	95·0 ,,	

In the earlier distillations, the sp. gr. of the first portions of alcohol that came over at 78·3° was distinctly higher than that of the later portions ; weaker alcohol was, in fact, being partially separated from stronger alcohol. In later distillations, when the dehydration was

more complete, this difference of sp. gr. was considerably less, and in the last two it was very small, although still noticeable.

The sp. gr. of the last and best fraction was nearly the same in the last four distillations, 0·80638, 0·80634, 0·80636, 0·80634 ; mean, 0·80635.

The only effect of the eighth distillation was to reduce the difference between the sp. gr. of the first and last fractions of alcohol, and the redistillation of this alcohol with more benzene produced no further change.   It seemed probable, therefore, that the whole of the water was removed, and that the slight difference in sp. gr. between the first and last fractions might be due to a very small amount of residual benzene, which, like water, would raise the sp. gr.

As already stated, n-hexane forms mixtures of constant boiling point with alcohol and with alcohol and water, and may be used for dehydrating alcohol. It possesses the advantage that the hexane-alcohol mixture can be separated very readily by distillation from the dehydrated alcohol.   Again, when hexane and benzene are distilled together, the hexane will carry down more than 10 per cent. of benzene without any rise of temperature, a mixture of minimum boiling point—a few hundredths of a degree below that of hexane—containing about 5 per cent. of benzene, being probably formed.

It seemed possible, then, that if alcohol dehydrated with benzene were distilled with hexane, any minute residual quantity of benzene would be carried down in the hexane-alcohol fraction, and that the hexane itself could be completely eliminated.   If, however, any hexane remained, the first fraction should have a lower sp. gr. than the last, since hexane is much lighter than alcohol.

A fresh quantity of alcohol was dehydrated with benzene, and 127·7 grams of this alcohol (sp. gr. 0·80638 at $0°/4°$) were distilled with 128·4 grams of n-hexane freshly distilled over phosphoric oxide.   The temperature remained quite constant at 58·65° for a long time, and when it changed, the rise to 78·3° was exceedingly rapid.   The alcohol was, as usual, collected in fractions, with the following results :

	Weight.		Sp. gr. at $0°/4°$.
1...................	22·3 grams.		0·80629
2...................	13·7	,,	—
3...................	30·0	,,	0·80627
Residue	8·8	,,	—
	74·8	,,	

The difference between the two sp. gr. was now practically within the limits of experimental error, although the tendency seemed to be still in the same direction.   The value 0·80627 may, I think, be taken

as very close indeed to the true sp. gr. of ethyl alcohol at $0°/4°$. It agrees very well indeed with the sp. gr. observed by Mendeléeff, $0·806254$, and the very low values observed by Squibb appear to be due to some chemical action of the lime on the alcohol, probably to the presence of a little ether.

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