XLV. *Theory of Ætherification.* *By* ALEXANDER WILLIAM-
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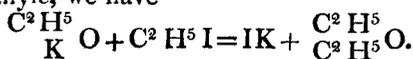versity*\*.

WHEN sulphuric acid is brought in contact with alcohol
under certain circumstances, a new arrangement is
effected in the elements of the alcohol, which divide into two
groups, forming æther and water. Now it is well known that
the process by which this change is effected may be repre-
sented in two ways, the difference of which consists in their
respectively selecting for starting-point a different view of the
constitution of alcohol. According to the one view, an atom
of alcohol weighs 23, and is made up of $C^2 H^6 O$; so that to
form æther, two atoms of it are needed, one of which takes
$C^2 H^4$ from the other, setting free the water with which these
elements were combined; whereas, according to the other
view, alcohol weighs 46, and *contains* æther and water. These
are not the only points of difference which are urged; but
they are the most real and tangible, and their consideration is
sufficient for our present purpose. If by any direct fact we
could decide which of these two expressions is the correct
one, the ground would be clear for an examination of the
process of ætherification itself. In order to show more clearly
the true meaning of the facts I have to adduce on this point,
I will bring them before you in the order in which they arose.

My object in commencing the experiments was to obtain
new alcohols by substituting carburetted hydrogen for hy-
drogen in a known alcohol. With this view I had recourse
to an expedient, which may render valuable services on similar
occasions. It consisted in replacing the hydrogen first by
potassium, and acting upon the compound thus formed by the
chloride or iodide of the carburetted hydrogen which was to
be introduced in the place of that hydrogen. I commenced
with common alcohol, which, after careful purification, was
saturated with potassium, and as soon as the action had ceased,
mixed with a portion of iodide of æthyle equivalent to the po-
tassium used. Iodide of potassium was readily formed on the
application of a gentle heat, and the desired substitution was
effected; but, to my astonishment, the compound thus formed
had none of the properties of an alcohol—it was nothing else
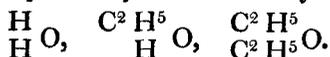than common æther, $C^4 H^{10} O$.

Now this result at once struck me as being inconsistent
with the higher formula of alcohol; for if that body contained
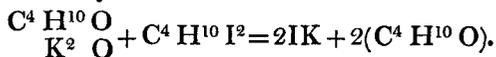twice as many atoms of oxygen as are in æther, I ought clearly

to have obtained a product containing twice as much oxygen as æther does. The alternative was evident; for having obtained æther by substituting $C^2 H^5$ for H in alcohol, the relative composition of the two bodies is represented *by expressing that fact in our formula.* Thus alcohol is $\begin{smallmatrix} C^2 H^5 \\ H \end{smallmatrix} O$, and the potassium compound is $\begin{smallmatrix} C^2 H^5 \\ K \end{smallmatrix} O$; and by acting upon this by iodide of æthyle, we have

$$\begin{smallmatrix} C^2 H^5 \\ K \end{smallmatrix} O + C^2 H^5 I = IK + \begin{smallmatrix} C^2 H^5 \\ C^2 H^5 \end{smallmatrix} O.$$

Of course the proportion between the two bodies is the only point upon which I here enter, and the same reasoning would be applicable to any multiple of the formulæ assumed. Some chemists may perhaps prefer doubling them in order to avoid the use of atoms of hydrogen, potassium, &c.; but I have not felt myself justified in doing so, because that would involve doubling the usual formula for water; for, as I will presently show, water is formed in ætherification by replacing the carburetted hydrogen of alcohol by hydrogen, which, of course, obliges us to assume the same unity of oxygen in both. Alcohol is therefore water in which half the hydrogen is replaced by carburetted hydrogen, and æther is water in which both atoms of hydrogen are replaced by carburetted hydrogen : thus,

$$\begin{smallmatrix} H \\ H \end{smallmatrix} O, \quad \begin{smallmatrix} C^2 H^5 \\ H \end{smallmatrix} O, \quad \begin{smallmatrix} C^2 H^5 \\ C^2 H^5 \end{smallmatrix} O.$$

This formation of æther might however be explained after a fashion by the other theory—by supposing the potassium compound to contain æther and potash, which separate during the action of the iodide of æthyle; so that half the æther obtained would have been contained in that compound, and the other half formed by double decomposition between potash and iodide of æthyle: thus—

$$\begin{smallmatrix} C^4 H^{10} O \\ K^2 \ \ O \end{smallmatrix} + C^4 H^{10} I^2 = 2IK + 2(C^4 H^{10} O).$$

But although the insufficiency of this explanation becomes evident on a little reflection, I devised a further and more tangible method of arriving at a conclusion. It consisted in acting upon the potassium compound by iodide of methyle, in which case I should, if that compound were æther and potash, obtain a mixture of æther and oxide of methyle; whereas in the contrary case I should obtain a body of the composition $C^3 H^8 O$. Now this substance I obtained, and neither æther nor oxide of methyle.

In this experiment the two theories cross one another, and must lead to different results; for it is evident that, in the first-mentioned decomposition by which æther was formed, the only difficulty in explaining the process decisively consisted in our inability to prove that the carburetted hydrogen introduced instead of the hydrogen did not have in the product an atom of oxygen to itself, but that, on the contrary, it was coupled with the carburetted hydrogen already contained in the alcohol—the two in combination with one atom of oxygen. It is clear that if alcohol *contain* æther and water, and the carburetted hydrogen in my first experiment formed a second atom of æther by taking the place of the hydrogen of this water, that the process being the same in the second experiment, we should then have obtained two æthers. Whereas if the formation of æther from alcohol be effected by synthesis, a new carburetted hydrogen being added to the one already contained in the alcohol, we ought to obtain the new intermediate æther which I obtained.

The complete description of this remarkable body, and of its decompositions, will form the subject of a future paper. I will now merely state that its boiling-point is a little above 10° Cent.; it is possessed of a very peculiar smell, distinctly different from that of common æther; and, like that body, it is only slightly soluble in water. It is not acted upon by the alkali-metals at the common atmospheric temperature.
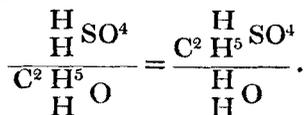
By acting upon the potassium-alcohol in like manner by iodide of amyle, I effected a similar substitution of the elements of that carburetted hydrogen in the place of the hydrogen of alcohol, and obtained an æther boiling at 111° C., having the composition $C^7 H^{16} O$. There is some reason to believe that this body is the same which Balard obtained by decomposition of chloride of amyle by an alcoholic solution of hydrated potash, and which that distinguished chemist took for oxide of amyle.

From the perfect analogy of properties between the known terms of the alcoholic series, it was to be expected that similar substitutions might be effected in the others; and I have verified this by experiment. Of course the formulæ of the other alcohols must be reduced to half, for the same reasons as that of common alcohol. Methylic alcohol is therefore expressed by the formula $\begin{matrix} C\ H^3 \\ H \end{matrix} O$, as common alcohol is $\begin{matrix} C^2\ H^5 \\ H \end{matrix} O$; and in the same manner amylic alcohol is $\begin{matrix} C^5\ H^{11} \\ H \end{matrix} O$, and the same of the higher ones. In conformity to this fact, we must be able to obtain the same intermediate æthers by replacing hydrogen in these alcohols (methylic and amylic) by the carbu-

retted hydrogen of iodide of æthyle, as by the inverse process described above. This I have verified in the case of the three-carbon æther, which may be obtained indifferently by replacing one-fourth of the hydrogen of methylic alcohol by $C^2 H^5$, or by replacing one-sixth of the hydrogen of common alcohol by $CH^3$. Its rational formula is therefore $\dfrac{C^2 H^5}{C \ H^3} O$.
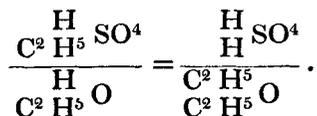
By acting upon the compound $\dfrac{C \ H^3}{K} O$ by iodide of amyle, I obtained a third æthereal compound, of which the formula is $\dfrac{C \ H^3}{C^5 \ H^{11}} O$. This is evidently the only one of the three new æthers, which, containing an even number of carbon atoms, might be conceived to have been formed from one alcohol; but when treated with monobasic acids, as hydrochloric, it cannot be expected to act in the same manner as its homogeneous isomeric, the æther $\dfrac{C^3 H^7}{C^3 H^7} O$ of the three-carbon alcohol $\dfrac{C^3 H^7}{H} O$; but of this I will give an exact account in the paper above alluded to.

My task is now to explain the process of ætherification by the action of sulphuric acid ($SO^4 H^2$) upon alcohol; and in order to accomplish that, I must show the connexion between those substances and the reagents used in the above-described experiments. With this view, I have merely to add to the above facts the acknowledged analogy of the simple and compound radicals in their compounds. I must first show how a substance analogous to my iodide of æthyle is formed, and then how by double decomposition with alcohol it produces æther. This is very easy; for sulphovinic acid is strictly analogous to iodide of æthyle plus iodide of hydrogen, which we should obtain by replacing $SO^4$ in its formula by an equivalent of iodine; and in order to represent the formation of this sulphovinic acid, which is well known to precede that of æther, the simplest mode is at the same time the one most free from hypothesis; it consists in stating the fact, that sulphuric acid and alcohol are transformed into sulphovinic acid and water, by half the hydrogen of the former changing places with the carburetted hydrogen of the latter: thus—

$$\frac{\dfrac{H}{H} SO^4}{\dfrac{C^2 H^5}{H} O} = \frac{C^2 \dfrac{H}{H^5} SO^4}{\dfrac{H}{H} O}.$$

Now from this point it is clear that the process is the same as in the decompositions above described; for by this sulphovinic

acid coming in contact with an atom of alcohol, it reacts exactly in the same manner as the iodide did, forming of course sulphuric acid and æther :

$$\frac{\begin{matrix} H \\ C^2\,H^5 \end{matrix}\,SO^4}{\begin{matrix} H \\ C^2\,H^5 \end{matrix}\,O} = \frac{\begin{matrix} H \\ H \end{matrix}\,SO^4}{\begin{matrix} C^2\,H^5 \\ C^2\,H^5 \end{matrix}\,O}.$$

The sulphuric acid thus reproduced comes again in contact with alcohol, forming sulphovinic acid, which reacts as before; and so the process goes on continuously, as found in practice.

We thus see that the formation of æther from alcohol is neither a process of simple separation, nor one of mere synthesis; but that it consists in the substitution of one molecule for another, and is effected by double decomposition between two compounds. I therefore admit the contact theory, inasmuch as I acknowledge the circumstance of contact as a necessary *condition* of the reaction of the molecules upon one another. By reducing the formulæ of the alcohols to one atom of oxygen, I also retain the equality of volumes which the contact theory insists upon between the vapours of these bodies and their æthers, so that æther truly contains the elements of olefiant gas in addition to those of alcohol in one atom. But, on the other hand, I attach equal importance to all the essential facts of the chemical theory, and rest my explanation of the process as much upon them as upon those of the contact theory; for, one-sixth of the hydrogen in alcohol truly exhibits different reactions from the remaining five, and must therefore be contained in that compound in a different manner from them ; and the alternate formation and decomposition of sulphovinic acid is to me, as to the partisans of the chemical theory, the key to explaining the process of ætherification.

Innovations in science frequently gain ground *only* by displacing the conceptions which preceded them, and which served more or less directly as their foundation; but, if the view which I have here presented be considered a step in our understanding of the subject, I must beg leave to disclaim for it the title of innovation; for my conclusion consists in establishing the connexion and showing the compatibility of views which have hitherto been considered contrary; and the best possible justification of the eminent philosophers who advocated either one of the two contending theories, is thus afforded by my reconciling their arguments with those of their equally illustrious opponents.

Before quitting the subject of ætherification, I would wish to add a few words on an application which naturally enough

suggests itself of the fact to which the process is here ascribed. I refer to the transfer of homologous molecules in alternately opposite directions, which, as I have endeavoured to show, is the cause of the continuous action of sulphuric acid in this remarkable process. It may naturally be asked, why do hydrogen and carburetted hydrogen thus continuously change places? It cannot be from any such circumstance as superior affinity of one molecule over another, for one moment sees reversed with a new molecule the transfer effected during the preceding one. Now in reflecting upon this remarkable fact, it strikes the mind at once that the facility of interchange must be greater the more close the analogy between the molecules exchanged; that if hydrogen and amyle can replace one another in a compound, hydrogen and æthyle, which are more nearly allied in composition and properties, must be able to replace one another more easily in the same compound; and that the facility of interchange of hydrogen and methyle, which are still more similar, will be still greater. But if this be true, must not the exchange of one molecule for another of *identical* properties be the most easily effected of all? Surely it must, if there be any difference at all; and if so, the law of analogy forbids our imagining the fact to be peculiar to hydrogen among substances resembling it in other respects. We are thus forced to admit, that, in an aggregate of molecules of any compound, there is an exchange constantly going on between the elements which are contained in it. For instance, a drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition Cl H, the proposition at which we have just arrived would lead us to believe that each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but, on the contrary, is constantly changing places with other atoms of hydrogen, or, what is the same thing, changing chlorine. Of course this change is not directly sensible to us, because one atom of hydrochloric acid is like another; but suppose we mix with the hydrochloric acid some sulphate of copper (of which the component atoms are undergoing a similar change of place), the basilous elements hydrogen and copper do not limit their change of place to the circle of the atoms with which they were at first combined, the hydrogen does not merely move from one atom of chlorine to another, but in its turn also replaces an atom of copper, forming chloride of copper and sulphuric acid. Thus it is, that at any moment of time in which we examine the mixture, the bases are divided between the acids; and in certain cases, where the difference of properties of the analogous molecules

is very great, it is found that the stronger acid and stronger base remain almost entirely together, leaving the weaker ones combined. This is well known in the case of a mixture of sulphuric acid and borax, and is a confirmation of our fundamental assumption, that the greater the difference of properties, the more difficult is the alternate interchange of one molecule for another.

But suppose now that instead of sulphate of copper, we mixed sulphate of silver with our hydrochloric acid in aqueous solution, and that a similar division of the bases between the acids established itself in the first moment, forming four compounds, $SO^4H^2$, $SO^4Ag^2$, $ClH$, $ClAg$; it is clear that this last-mentioned compound, being insoluble in water, must, on its formation, separate out and remove from the circle of decompositions which solubility established. But of course the three compounds remaining in solution continue the exchange of their component parts, and give rise successively to new portions of chloride of silver, until as much of that compound is precipitated as the liquid contained equivalents of its component parts, a very small quantity remaining in solution and in the circle of decompositions.

Such is the general process of chemical decomposition. Of course a compound is removed as effectually from the circle of decompositions by possessing the gaseous form under the circumstances of the experiment, or even by being a liquid insoluble in the menstruum. I believe this explanation coincides in its second part with the one proposed many years ago by Berthollet; but not making use of the atomic hypothesis, upon which my explanation is based, that eminent philosopher went no farther back than the division of the acids between the bases on the mixture of salts, a fact which I have here deduced from the motion of atoms. It is well known that the general fact upon which Berthollet founded his view is denied by some eminent chemists of the present day; but I believe the instances which they adduce are only apparent exceptions to the law, and will on further examination be found to afford additional confirmation of the truth of the great Savoysien's conception, as I have shown in the case of boracic and sulphuric acids.

In using the atomic theory, chemists have added to it of late years an unsafe, and, as I think, an unwarrantable hypothesis, namely that the atoms are in a state of rest. Now this hypothesis I discard, and reason upon the broader basis of atomic motion.