

OBITUARY NOTICES.

Professor A. W. Williamson. By Professor
A. Crum Brown.

(Read January 8, 1906.)

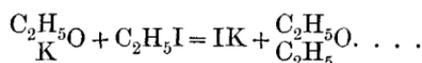
Alexander William Williamson was born at Wandsworth, May 1st, 1824. He studied chemistry under Gmelin in Heidelberg and under Liebig in Giessen, where he graduated as Ph.D. In 1848 he studied mathematics under Comte in Paris. In 1849 he was appointed Professor of Practical Chemistry in University College, London; and in 1855, in addition, Professor of Chemistry. He was elected Fellow of the Royal Society of London in 1855, and was Foreign Secretary of the Society from 1873 to 1889, and Vice-President in 1889, 1890. He was President of the British Association in 1873. He was elected Hon. Fellow of this Society in 1883. In 1887 he resigned his chair and retired to Haslemere, where he died May 6th, 1904.

Williamson's chemical work was not great in quantity, but was of the very highest importance, and his name will always remain in the history of chemistry in the list of the great leaders.

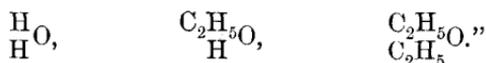
Berzelius gave H_2O as the formula of water, but the duplicity of the hydrogen in this formula was deduced from physical considerations only, and was not used to explain any chemical phenomena. The chemical unit of hydrogen was to Berzelius and his followers the "equivalent" H_2 and not the atom H , and they wrote hydrochloric acid and ammonia H_2Cl_2 and N_2H_6 , until a special symbol, a barred letter, was invented for the equivalent in the case of each element the equivalent of which consisted of two atoms. It was Williamson who brought to light the chemical meaning of the 2 in H_2O , and showed that these two atoms are not permanently tied together, but are each separately united to the one indivisible atom of oxygen.

By the action of potassium on alcohol one-sixth of the hydrogen

of the alcohol is removed and a compound formed containing potassium in the place of this hydrogen. It occurred to Williamson that if this potassium alcohol were treated with the halogen compound of a hydrocarbon radical the potassium and the halogen would unite, and a new and more complex alcohol be formed containing the hydrocarbon radical in place of the potassium, and therefore in place of the hydrogen which had been removed by the action of the potassium. This idea was the foreshadowing of a very important method of synthesis, but the result showed that it was not applicable in this case. By acting on potassium alcohol with ethyl iodide Williamson obtained indeed potassium iodide, but the other product was not a new alcohol but common ether. He at once saw the explanation of this. He regarded alcohol not as a compound of ether and water, the common view at that time, but as an intermediate substance, not $\text{Ae}_2\text{O}, \text{H}_2\text{O}$, but AeHO , in which the ethyl and the hydrogen are independently united to the one atom of oxygen, and he recognised that it is this hydrogen and not hydrogen of the C_2H_5 that is replaced by potassium. "Thus alcohol is $\text{C}_2\text{H}_5\text{O}$, and the potassium compound is $\text{C}_2\text{H}_5\text{O}$; and by acting upon this by iodide of ethyl we have



Alcohol is therefore water in which half the hydrogen is replaced by carburetted hydrogen, and ether is water in which both atoms of hydrogen are replaced by carburetted hydrogen, thus :



But as the formation of ether in this way could be explained on the supposition that alcohol is a compound of ether and water, and potassium alcohol a compound of ether and oxide of potassium, half of the ether produced being that united with oxide of potassium and the other half coming from the action of the oxide of potassium on the ethyl iodide, Williamson devised and carried out a crucial experiment. By acting on potassium ethylate with methyl iodide and on potassium methylate with ethyl iodide he obtained in both cases the same product, which was not a

mixture of the two ethers but an intermediate ether $\begin{matrix} \text{C}_2\text{H}_5\text{O} \\ | \\ \text{CH}_3 \end{matrix}$. In a similar way he prepared the intermediate amyl-methyl and amyl-ethyl ethers. He then goes on to use these principles to explain the ordinary process for preparing ether, giving the sequence of actions now familiar to every student of chemistry, and showing experimentally that three ethers are formed when a mixture of two alcohols is distilled with sulphuric acid.

Williamson's work on etherification was published in a paper read before the Chemical Section of the British Association at its meeting in Edinburgh in 1850 and printed in the *Philosophical Magazine*. It is in this paper that the following striking passage occurs:—"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 amyl can replace one another in a compound, hydrogen and ethyl, 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 methyl, 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 ClH , 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."

The observed facts of balanced actions of double decomposition led Williamson to this view, and it is interesting to note that the observed facts of electrolysis led Clausius quite independently to a somewhat similar hypothesis about seven years later.

A paper read before the Chemical Society of London, June 1851, contains, besides further details as to the preparation, analysis, and vapour density of the new intermediate ethers, a very important note on the constitution of acetone, and an account of an intermediate ketone, with a very clear statement of the constitution of these bodies and a forecast of the general method of preparing aldehydes afterwards independently discovered by Limpricht and by Piria.

In a paper in the *Chemical Gazette*, 1851, he points out the analogy between ether and the anhydrous monobasic organic acids, then unknown, but soon afterwards discovered by Gerhardt, who obtained them by a process perfectly analogous to that used by Williamson for the preparation of the ethers.

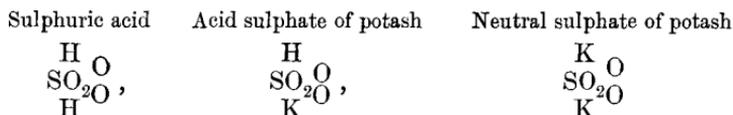
As Williamson had thus, in 1850, established the "water type" on a secure experimental basis, so, in 1854, he extended similar reasoning and demonstration to the case of sulphuric acid, and showed how dibasic acids and their derivatives can be referred to the double type of water.

In a paper communicated to the Royal Society of London he writes:—"An atom of nitric acid, being eminently monobasic, is, as we have already shown, represented in the monobasic type $\frac{\text{H}}{\text{H}}\text{O}$ by the formula $\frac{(\text{NO}_2)}{\text{H}}\text{O}$, in which peroxide of nitrogen (NO_2) replaces one atom of hydrogen. In like manner, hydrate of potash $\left(\frac{\text{H}}{\text{K}}\text{O}\right)$ is obtained by replacing one atom of hydrogen in the type by its equivalent of potassium; and nitrate of potash $\left(\frac{\text{NO}_2\text{O}}{\text{K}}\right)$ by a

simultaneous substitution of *one* atom of hydrogen by peroxide of nitrogen, the *other* by potassium. Sulphuric acid is formed from

two atoms of water $\begin{matrix} \text{H} \\ \text{O} \\ \text{H} \\ \text{O} \\ \text{H} \end{matrix}$; one of hydrogen from each is removed,

and the two replaced by the indivisible radical SO_2 . The series



explains itself."

He then describes the action of pentachloride of phosphorus on sulphuric acid:—"Confining my remarks for the present to the case of sulphuric acid, whose decomposition is doubtless typical of that of other bibasic acids, I may state as the result of numerous experiments with the most varied proportions of pentachloride and acid, performed on a scale of considerable magnitude, that the first action of the pentachloride consists in removing one atom of hydrogen and one of oxygen (empirically peroxide of hydrogen) from the acid, putting in an atom of chlorine in their place, and

forming the compound $\begin{matrix} \text{H} \\ \text{SO}_2 \\ \text{Cl} \end{matrix}$ O, which is strictly intermediate be-

tween the hydrated acid and the final product SO_2Cl_2 formed by a repetition of the same process of substitution of chlorine for peroxide of hydrogen. The existence and formation of this body, which we may call chloro-hydrated sulphuric acid, furnishes the most direct evidence of the truth of the notion, that the bibasic character of sulphuric acid is owing to the fact of one atom of its radical SO_2 replacing or (to use the customary expression) being equivalent to two atoms of hydrogen. Had this radical been divisible like an equivalent quantity of a monobasic acid, we should have obtained a *mixture*, not a *compound*, of the chloride with the hydrate,—or, at least, the products of decomposition of that mixture."

In another paper in the same volume of the *Proceedings* we find the following:—"According to the results of recent researches in the constitution of salts and the method thence introduced of

explaining chemical reactions, it is equally correct to represent such a reaction as that of hydrochloric acid on hydrate of potash, as consisting in an exchange of hydrogen of the one for potassium of the other, or of chlorine in one for peroxide of hydrogen in the other. In Mr Kay's researches, as described in the following brief outline, this notion has obtained very striking illustrations; for he has obtained a peculiar body in which the chlorine of chloroform is replaced by peroxide of ethyle by the action of chloroform on three atoms of ethylate of sodium, which product may be equally well conceived to be a body in which the hydrogen of three atoms of alcohol is replaced by the tribasic radical of chloroform. According to the older theories of the capacity of saturation of salts, this compound would contain a tribasic modification of formic acid, for it has the same relation to formic ether as a so-called tribasic phosphate has to a monobasic one."

It will be seen from the examples referred to that the leading principle of Williamson's work was the then quite novel idea of the "atomic value" of radicals, which is exactly what we now call their valency, and that his favourite method was the formation of intermediate substances as a guide to a knowledge of the constitution of the bodies between which they lie. This principle and this method led in Williamson's hands to important development and simplification of chemical theory, and they still bear good fruit.

Williamson's influence on the progress of chemistry is not to be measured only by the work done directly by him; every chemist who had the privilege of being his friend knows how much of his clear, intelligent knowledge of chemistry is due to Williamson.