

again increasing the pressure to 73 atmospheres. On now rapidly letting down the temperature to 15° C. a white mass of camphor separated out from the liquid, which again dissolved on a slight increase of pressure, although it could not be again separated out by diminishing it. These actions may be due, in part, to supersaturation and the effect of pressure in aiding solubility when contraction takes place during solution.

These experiments show that carbonic acid at high pressures in presence of various substances acts as if it produced a series of unstable chemical compounds, which are decomposed and recomposed according to the conditions of temperature and pressure in the medium. Further observations are required to elucidate many obscure actions taking place under such conditions of experimenting as are detailed in the above communication.

IV. "The Aluminium-Iodine Reaction." By J. H. GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, F.C.S., Lecturer on Chemistry in Dulwich College. Received June 10, 1880.

About four years ago we pointed out a reaction of iodide of aluminium which, as far as we are aware, has no precise analogue in the science of chemistry, and which has led to the discovery of several volatile aluminium alcohols. It is well known that neither water, alcohol, nor ether is decomposed by metallic aluminium, and that each of these bodies will dissolve iodine without entering further into combination with it; but we found that by the joint action of these two elements, it was possible to split up the above-mentioned liquids. Water, though forming a definite hydrate with the iodide of aluminium, is decomposed by it in the presence of an excess of the metal, hydrogen being evolved and aluminic hydrate formed. This takes place at the ordinary temperature.

Alcohol in a similar manner is decomposed by the joint action of metallic aluminium and its iodide, with the ultimate production of hydrogen gas, aluminic ethylate, and varying amounts of aluminic iodoethylate proportional to the quantity of aluminic iodide employed. A small quantity of the iodide suffices to bring about the formation of a very large amount of the ethylate; in fact, the process would be a continuous one, were it not that the solid products gradually put a stop to the reaction.

Ether is not affected by aluminic iodide and aluminium, but when exposed to iodine and aluminium simultaneously it suffers a violent decomposition, iodide of ethyl and the aluminic iodoethylate being the ultimate products.

Amylic ether behaves in a similar manner, and the acetates of ethyl and amyl give analogous results; but the reaction is not an ordinary

double decomposition, for it does not take place when ready-formed iodide of aluminium is employed.

The several changes thus described are typical of our "aluminium-iodine reaction." The reaction is quite distinct from that which has lately given beautiful results in the hands of Friedel; and we have investigated its applicability both for the production of new compounds, and for distinguishing between different classes of organic bodies, as well as for throwing light on their comparative constitution.

Neither zinc nor iron, nor, as far as we know, any other metal can be substituted for aluminium in this reaction; but the chloride or bromide may be used instead of the iodide, though with less advantage.

Recent Results.

For decomposing an alcohol a small quantity of iodine is dissolved in it, the necessary excess of aluminium is added, and the mixture is heated. Evolution of hydrogen gas begins immediately, and proceeds somewhat rapidly until the whole of the metal has passed into combination. In this way the aluminium derivatives of the following alcohols have been prepared:—Ethylic, normal propylic, iso-butylic, amylic, benzylic, phenylic, cresylic, and thymolic. The first four of these aluminium derivatives may be distilled *in vacuo*, and they have thus been separated from the other solid products of the reaction, and obtained in a pure condition. The other aluminic alcohols cannot be distilled, at any rate not without very considerable decomposition. The following alcohols, however, behaved in a different way with the reagent:—

Methyl alcohol is not decomposed by aluminic iodide and aluminium, but in presence of free iodine it parts slowly with hydrogen, and the same happens when an aluminium-platinum couple is substituted for the metallic aluminium.

Iso-propyl alcohol.—This is not acted upon in the least by the reagents.

Cetyl alcohol.—On heating this compound with the reagent, hydrogen is slowly set free, until the temperature reaches about 200° C., when another chemical change is set up, resulting in the formation of cetyl iodide and aluminic hydrate.

Allylic alcohol.—The first action is identical in character with that which takes place with the alcohols of the $C_nH_{2n+1}OH$ series. Instead, however, of the whole of the liberated hydrogen escaping, about 30 per cent. of it acts upon the excess of alcohol, splitting it up into propylene and water.

Ethene alcohol.—The reagent does not liberate hydrogen from this substance, and has but a very slight action upon it.

Propenyl alcohol.—No hydrogen is evolved, but a double decomposition ensues at about 140° C., yielding allyl iodide, free iodine, and

aluminium hydrate; if aluminium be in excess, aluminic hydrate and allylic iodide are the sole products.

Aldehyde.—Hydrogen is not set free from this compound.

The general result, then, of these observations is that the reagent substitutes aluminium for the basic hydrogen of water, and of all the alcohols hitherto tried, whether of the methyl, allyl, benzyl, or phenyl series, with the remarkable exception of isopropyl alcohol. On the other hand, it does not substitute aluminium for hydrogen in the dihydric or trihydric alcohols, nor yet with aldehyde. The reaction with the ethers and glycerine is of a different character, as, in addition to an aluminium compound, the iodides of the positive radicals are formed.

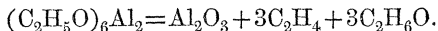
General Properties of the Aluminium Alcohols.

The aluminium alcohols are solid at the ordinary temperature, and fuse generally into clear liquids. They possess, in a marked degree, the property of remaining fluid far below their melting points. Those of the methyl series distil unchanged at reduced pressures, affording the first organic compounds which contain both oxygen and a metal and are capable of distillation. They are soluble more or less in ether, alcohol, and benzol, but are decomposed by water with the formation of aluminium hydrate and the alcohols.

They were found to have the following specific gravities at 4° C. :—

Ethylate	1.147	Phenylate	1.25
Propylate	1.026	Cresylate	1.166
Butylate	0.982	Thymolate	1.04
Amyleate	0.980		

Action of heat.—All these alcohols are decomposed at a temperature somewhere about their boiling points, and it became an interesting subject of inquiry whether they were resolved into alumina, and the alcohol and its olefine, or into alumina and the ether. Both these actions seem to take place. Thus aluminic ethylate appears to be decomposed by heat in both ways, but mainly according to the following scheme :—



Aluminic phenylate on the other hand is capable of decomposition mainly in the following way :—



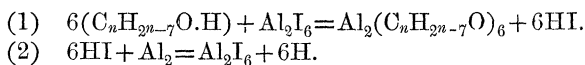
It must not however be supposed that these decompositions take place without other reactions. Some of the bodies thus produced are new ones, and we are at present engaged in their investigation.

The most interesting decomposition is that of the thymolate. When

heated it splits up into alumina, propylene, and bodies of the cresylic group. One of these is a solid body, which when resublimed or crystallised from alcohol presents itself in most beautiful pearly plates. Its properties resemble rather those of an ether, and concordant analyses of different specimens and determinations of vapour density give the anomalous molecular formula $C_{14}H_{13}O$, but its real constitution is still the subject of inquiry.

Theory of Reaction.

The reaction by which the compounds described above are formed is by no means clear at first sight. It is difficult to imagine that the presence of a haloid salt should determine the direct replacement of hydrogen by aluminium in water or in alcohol. We believe however that the presence of hydriodic acid in the reaction with the aromatic alcohols furnishes the true key to the chemical change. The first action is in all probability that of a reciprocal decomposition between two binary compounds—the alcohol and aluminium iodide—forming a certain proportion of aluminium alcohol and hydriodic acid. But the metallic aluminium present at the same time decomposes the hydracid with evolution of hydrogen and the production of more aluminium iodide, which brings about a further redistribution of the elements and the formation of more of the aluminium alcohol and the hydriodic acid, and so on till the chemical change is complete. The following equations express these changes, which take place alternately or rather continuously:—



It is evident that as the iodine does not enter into the final products a very small quantity of it is sufficient to carry on the continuous chemical change.

There can be little doubt that the same reactions occur in the case of the alcohols of the $C_nH_{2n+1}O.H$ series, but the amount of hydriodic acid formed in the reciprocal decomposition is perhaps very small, and the tenacity with which it is held by the alcohol has made it impossible for us to prove its separate existence. The same remark applies also to water, which we believe to act in the same way. Indeed we know from the experiments of Roscoe that there would be no chance of separating minute quantities of acid from an aqueous solution under the circumstances.

The part which the free elements take in the decomposition of the ethers is doubtless analogous to that which the combined elements play in the action with water and alcohol. The reason why the free elements do, and aluminic iodide does not attack the ethers, is probably

owing to the available energy being greater in the former than in the latter case.

In conclusion, we would commend this aluminium-iodine reaction to the consideration of other chemists, who may be investigating organic compounds containing oxygen.

V. Preliminary Note on the Ossification of the Terminal Phalanges of the Digits." By E. A. SCHÄFER, F.R.S., and F. A. DIXEY, B.A. Received June 3, 1880.

The diaphyses of the ungual phalanges of the digits offer an exception to the usual mode of ossification of diaphysial bones (including the other phalanges) in the fact that the calcification of the cartilage and its attendant changes begins at the tip and not in the centre of the diaphysis. The subperiosteal intramembranous ossification also commences at the same point—the tip, namely, of the cartilage—as a cap-like expansion over the end of the cartilage. The irruption of the osteoblastic subperiosteal tissue also first occurs here, so that this part seems to correspond morphologically with the centre of the shaft of other long bones. The expanded portion of the phalanx which bears the nail, claw, or hoof, is entirely formed by an outgrowth of the subperiosteal bone, and is not preceded by cartilage.

A detailed account of the mode of ossification of these phalanges will be shortly published.

VI. "On the Organisation of the Fossil Plants of the Coal-measures. Part XI." By W. C. WILLIAMSON, F.R.S., Professor of Botany in the Owens College, Manchester. Received June 3, 1880.

(Abstract.)

M. Renault has recently published a memoir, in which he reproduces the views of M. Brongniart respecting the relations which the *Lepidodendra* bear to the *Sigillariæ*, still insisting that the former are cryptogamic Lycopods, whilst the latter are exogenous Gymnosperms. In endeavouring to establish this position, the French palæo-botanist concludes that if the exogenous *Diploxyloid* stems (*i.e.*, *Sigillarian* ones) are but matured states of some *Lepidodendra*, every *Sigillarian* type of organisation ought to be found in a young or *Lepidodendroid* form, because, he contends, the type of the central organisation, once established, undergoes no further change with advancing age. In support of his position, he affirms that there are three such *Sigillarian*