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HISTORY OF THE ORGANIC RADICALS.

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Translated from the French, by W. S. W. Ruschenberger, M. D., U. S. N.

Gentlemen: I propose to set forth in a summary manner in this lecture the history of organic radicals, the study of which, though dating back scarcely thirty years, has produced fruitful results, and contributed largely to the development of organic chemistry.

We give the name of radicals to particular compounds, whose complex nature may be rendered evident by the aid of physical forces, or by the intervention of reagents; but which, though formed of many elements, present the characters of simple bodies and exercise functions precisely similar. They are, in a word, compounds, which possess the property of forming with simple bodies, combinations entirely analogous to those which the latter produce by their mutual union.

Among the radicals some are known in the isolated state; these may be handled and made to combine and to separate under influences which enable us to make and unmake chemical compounds of most varied character, such as cyanogen, cacodyl, stibethyl, &c.; but the greatest number, it must be admitted, have only a purely hypothetical existence. Among the latter are methyl, ethyl, acetyl, benzöile, ammonium, &c.

By grouping the different organic compounds into families or determinate series of which each includes a fixed nucleus or radical, a kind of pivot around which all bodies of the group turn, their study has been considerably simplified, rendering them both more advantageous and philosophic. Thus in the alcohol derived from wine, the ether of pharmacy, and the different compound ethers, chemists have admitted the existence of a fixed group,

$$C^4H^5$$

analogous to potassium, although up to the present time we have been unable to isolate a product presenting this composition, which would be capable of forming ordinary ether by its direct union with oxygen, or of engendering chlorohydric ether, by combining it with chlorine. By causing zinc to act on iodohydric ether in closed vessels at a temperature of from 140° to 150° [centigrade,] M. Frankland separated iodine in the state of a metallic iodide, and was enabled to collect a compound gas formed of 4 eq. of carbon+5 eq. of hydrogen.

But this, the formula of which it is necessary to double in order to place its equivalent in harmony with those of all well defined compounds, although offering us in reality the composition of the product designated under the name of ethyl, presents none of the characters which a radical should possess.

Placed in the presence of chlorine, far from reproducing chlorohydric ether, as we should expect, it furnishes, as is observed in different hydrogenous compounds, a product derived by substitution. Oxygen, in whatever condition it may be made to intervene, will not effect its conversion into ordinary ether. I would say as much of the product obtained in treating benzöine by chlorine, a compound which Laurent considered as the radical of benzöic combinations, as the true benzöile, as well as of the other isomeric, the formation of which has been indicated in the dry distillation of the benzoate of copper.

If then we study attentively these diverse groupings which have been regarded as radicals, we shall not be slow to perceive that only a very small number of them satisfy the conditions, which similar products ought to satisfy, namely: to beget by their union with certain simple bodies clearly definite compounds, from which they might be afterwards separated perfectly intact. If we see certain groupings, which we suppose to constitute the nucleus of a given substance, pass into the numerous compounds it is susceptible of forming, or into different derivatives which contact with reagents may produce, that is not sufficient evidently to range them in this group of bodies; such are ethyl, benzöile, &c., of which we spoke before. Certainly the study of all these bodies is most instructive, and it will not be denied that to the profound examination of these questions, organic chemistry is indebted for the great strides it has made in latter years, so much have observers multiplied experiments to elucidate them; nevertheless, it seems to me more suitable in the actual state of science, to consider as radicals only those singular substances, which, taken in a pure state, behave in the manner of simple bodies.

Such definite grouping appears to us most frequently as a radical, only according to the particular view we take, or according to the metamorphoses determined by the reagent we employ. Thus if we consider the formation of acetic acid by the oxidation of alcohol, or, better, of aldehyd, we are led to regard this product as the oxide of a ternary radical which we designate under the name of acetyl, but if we base our view upon the decomposition which this same acid undergoes on the part of alkaline bases, at elevated temperatures or on the separation which electrolysis effects in it, we are naturally brought to trace its derivation to the reciprocal action of carbonic acid, and the grouping C^2H^4, which is nothing but marsh gas. From this we might express the constitution of acetic acid by the aid of the formulæ,

$$\left.\begin{array}{c} C^4H^3O^2 \\ H \end{array}\right\} O^2,$$

$$C^2O^3,\ C^2H^3,\ HO.$$

both of which satisfy clearly definite reactions.

It is now known that acetic acid may be produced, either by the direct oxidation of aldehyd, or the decomposition of the chloride of acetyl by water, or by the contact of carbonic acid with *kalimethyl* or *natrimethyl*.

It is what is expressed by the equations

$$\begin{array}{c} C^4H^3O^2 \\ H \end{array} + O^2 = C^4H^4O^4$$

Aldehyd. *Acetic acid.*

$$\begin{array}{c} C^4H^3O^2 \\ Cl. \end{array} + HO = C^4H^4O^4 + HCl.$$

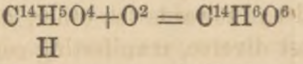
Chloride of acetyl. *Acetic acid.*

$$C^2O^4 + C^2H^3Na = C^4H^3NaO^4$$

Natrimethyl. *Acetate of soda.*

It would be the same with all the acids of the acetic group. Now, whatever may be the veritable constitution of these different acids, of which we are entirely ignorant in the present state of science, there remains no less knowledge of them, on account of the close analogies which connect these bodies to each other; if we had just discovered the real constitution of one of them, we should easily understand that of others, and there is consequently a very great advantage in arranging them in the same series, a knowledge of all flowing from that of a single one.

I would say as much of salicylic acid and its homologues, this acid being as readily obtainable by the oxidation of the oil of spiræa as by the action of carbonic acid upon the phenate of sodium. In fact, we have



$$\underset{H}{C^{14}H^5O^4}+O^2 = C^{14}H^6O^6$$

Oil of spiræa. Salicylic acid.

$$C^2O^4+C^{12}H^5NaO^2 = C^{14}H^5NaO^6$$

Phenate of sodium. Salicylate of soda.

In place, then, of regarding aldehyde and oil of spiræa as hydrurets of ternary radicals, acetyl and salicyl, which we have been unable to seize, and, consequently, acetic and salicylic acids as oxides of these radicals, is it not more simple to consider them, with M. Dumas, as types in which we may, by the aid of double decompositions, effect a series of regular substitutions, without destroying their equilibrium, without modifying their mechanical grouping. We find ourselves in this way brought back to the equivalent compositions of M. Chevreul, which, prejudging nothing, permits the observer to try such reaction as may appear to him realizable from his point of view; these equivalent compositions presenting besides the great advantage of offering us a register by which to verify our analyses or permitting us to seize upon relations which without them would remain unperceived.

We will, therefore, restrict the name radical to compound bodies which, taken in the free state, such as cyanogen, cacodyl, stibethyl, and their analogues, &c., possess the characters of true simple bodies playing sometimes the part of an electro-negative element or supporter of combustion, sometimes that of an electro-positive element or combustible.

I propose to examine only those in this lecture, not that I think that some of these hypothetical bodies may not be isolated at some future time, but because it appears to me more suitable to consider such only as it is possible to obtain in a free state.

This stated, I will now endeavor to demonstrate the simple idea I entertain of the part played by these curious bodies, however singular it may appear at first, and which seems to me to be naturally derived from the law of chemical combinations.

If we place in presence of each other two elements, endowed with a mutual affinity in greater or less degree, they will be evidently attracted one towards the other, and will give rise to compounds the most diverse, manifesting certain physical phenomena, such as the development of electricity, of heat, and sometimes of light, the intensity of which will depend upon their degree of affinity. Be this as it may, these bodies are incapable of uniting in all imaginable proportions, and daily experience demonstrates in the most evident manner that in this contact, however varied may be the circumstances under which it is effected, they can never form but a very limited number of combinations. If the affinities which solicit these bodies are very energetic, they form at most two or three compounds, most commonly only one, and these always oppose great resistance to decomposition. The manner in which hydrogen and the alkaline metals behave with chlorine; the products which result from the contact of charcoal, of boron, of silicium, &c., with oxygen at high temperatures, demonstrate it sufficiently. On the contrary, bodies which have little tendency to unite when placed in presence of each other, form numerous, but always unstable compounds. To enable us to be understood, we think it is enough to refer to the history of the oxygenated compounds of chlorine.

In every case, whatever may be the number of compounds which two simple bodies may be susceptible of forming by their mutual union, there is always one which possesses greater stability than the others, and towards which they all converge.

But the greater or less stability of such group is evidently only relative to the special circumstances under which its formation is effected. Hence, whenever we place in very determinate conditions the different compounds which two bodies have produced by their mutual union, they constantly assume the particular form which is alone possible in these conditions. We all know, for example, that of all the compounds which phosphorus is susceptible of forming with oxygen, the most stable is phosphoric acid. Under special influences phosphorus may be united to this gas in other proportions, but all these different compounds converge towards this group under the influence of high temperature. Acted upon in the presence of free oxygen, there will be a fixation of a certain quantity of this gas. Acted upon in closed vessels, there will be a separation of a certain quantity of phosphorus. In all cases, whenever phosphorus does not assimilate the proportion of oxygen necessary for its transformation into phosphoric acid, it may be always brought back to this form, or substituted in place of a portion of this oxygen, other simple bodies, such as of chlorine, bromine, sulphur, &c., so as to produce the compounds known under the names of chloroxide, bromoxide, and sulphoxide of phosphorus, which, the same as phosphoric acid, belong to the group

$$PhX^5.$$

In a word, when we place in presence of each other two simple bodies, susceptible of uniting under determinate conditions, and of giving rise to many definite compounds, we observe that there always exists a state of saturation which possesses an equilibrium that it is impossible to exceed. As long as this state of equilibrium is not attained, we may add to the first body a new proportion of the second until saturation is effected.

There are certain bodies which, by uniting with another, yield very stable products which, not having reached the point of saturation, have a tendency to combination quite as great and sometimes even more energetic than the simple bodies themselves. Such are carbon, sulphur, and nitrogen; oxide of carbon, sulphurous acid and binoxide of nitrogen, being susceptible not only of absorbing new quantities of oxygen with greater facility than the simple bodies which they contain, but of also uniting with chlorine and iodine, to form compounds corresponding to those which are at the maximum of oxygenation. These very stable groups, which may be made to enter into definite compounds, to be afterwards separated from them without undergoing the slightest alteration, and those alone which thus present the fundamental properties of simple bodies, truly merit the name of radicals.

We may easily conceive the sensation produced by the discovery of cyanogen, which, so long as it is not altered in its elementary constitution, presents in a faithful manner the most prominent properties of chlorine and its congeners. We can now give a very clear account of the remarkable functions of cyanogen in setting out from combinations with nitrogen.

Every compound may be considered as a molecular system in equilibrium in which the atoms are attracted towards each other in virtue of more or less powerful affinities. If we replace one or more atoms of one of the elements of the compound by an equal number of atoms of another substance, we obtain a new compound which will present the same mechanical grouping as the primitive product, but whose state of equilibrium within extended limits, is accordingly as the reciprocal attractions of the bodies which constitute the new substance shall be more or less energetic than those of the primitive bodies. Ammonia being susceptible of exchanging all or part of its hydrogen for chlorine, bromine, iodine, carbon, cyanogen, ethyl, the metals, &c., should necessarily form, by means of these substitutions compounds belonging to the same system, but presenting the most diverse conditions of equilibrium; this is demonstrated in the most evident manner by experience.

It is thus that although ammonia resists a dull red heat, we clearly understand that chloride of nitrogen may be instantly destroyed, not only by the effect of temperatures below the boiling point of water, but under the influence of the slightest disturbance, the affinities which solicit chlorine and nitrogen being incomparably weaker than those which unite the latter to hydrogen.

If now we remove an atom from the primitive group without replacing it, and if the new combination which results from this elimination presents a certain stability, it may fix anew the atom of the substance eliminated, to reproduce the primitive body or an atom of any other simple body to produce compounds of the same type; the compound formed under these circumstances will act from that moment as a true radical. Let us pass a current of dry ammoniacal gas over charcoal arranged in a porcelain tube brought to a red heat, two atoms of hydrogen will be eliminated, two atoms of carbon will take their place, and we shall obtain cyanhydric acid, a compound the grouping of which corresponds to that of ammonia, but whose properties are very different, as may be readily conceived, the chemical functions of carbon being very different from those of hydrogen.

By its reaction upon the oxides of mercury or silver, cyanhydric acid thus produced will give rise to the formation of cyanurets which will not differ from it except that the molecule of hydrogen will be found replaced in it by a molecule of metal, silver or mercury, but the fundamental characters will be still evidently the same. If we now subject these cyanurets to the action of increasing temperatures, a moment will soon arrive when equilibrium is no longer possible, and we shall see a separation into a metal which will remain as residue in the distillatory apparatus, and a gas, the composition of which is expressed by the formula.

$$AzC^2. \qquad [NC^2.]$$

This gas is no other than cyanogen, which to enter into the ammonia type has but to *fix* an atom of different simple bodies, playing in respect to them sometimes the part of an electro-positive element, as in cyanic acid and chloride of cyanogen, and sometimes the part of an electro-negative as in cyanhydric acid and the cyanurets. This cyanogen which just now could not exist in combination with mercury or silver at a dull red heat, on account of its feeble affinity for those bodies, when heated under a bell glass with potassium, manifests vivid ignition, giving rise to the compound

$$AzC^2K \ [NC^2K.]$$

belonging, like the preceding, to the type

$$AzX^3 \ [NX^3,]$$

but this time capable of resisting very high temperatures. If cyanogen thus perfectly simulates the characters of a true simple body, it is evidently due on the one hand to its considerable stability, and on the other to its tendency to produce combinations at the maximum of saturation which are themselves very stable, by assimilating a molecule of some simple body to enter again into the primitive type from which it was derived. The part of cyanogen as a radical, as a body acting in the character of an element, is so explained in a most satisfactory manner; we shall see that the same is true of various products known under the name of radicals.

When we place a simple body, metal or metaloid, in presence of oxygen, it forms with this gas, as we have seen, definite compounds in various numbers; replace the oxygen by chlorine, bromine, sulphur, &c., and we beget compounds represented by parallel formulæ; now experience shows, that adopting suitable processes we can form with this same body and methyl, or any one of its homologues, products whose composition is entirely comparable. Methyl or its homologues united to electro-negative bodies which are at the top of the scale of simple bodies, (oxygen, chlorine, bromine, iodine, &c.,) yield very stable compounds, which possess perfect neutrality. In proportion as we descend the scale, and advance towards potassium which forms the lowest point of it, we obtain products whose affinity for simple bodies which occupy its superior extremity goes on increasing to such a point that, when it reaches the group of alkaline metals, there is a dislocation of the molecule and formation of very simple and consequently very stable products.

If we unite methyl with the intermediate bodies we shall obtain compounds that still possess a great affinity for oxygen, chlorine, &c., and consequently capable of forming with these bodies clearly definite compounds whose stability is such that they may be completely separated from them intact. In this way may be produced bodies comparable to cyanogen, at least as long as the proportion of methyl or of ethyl which enters into the composition of these products represents the term of saturation, in which case, it is believed, the molecule is entirely inapt to enter into combination.

When a simple body A forms with another simple body B, several compounds, whose term of saturation is represented by the formula

$$ABx.$$

(x being a whole number always very simple,) experience demonstrates that we may form with this body A and the different alcoholic radicals compounds at different states of saturation. As long as the number of molecules of the alcoholic radical which enters into the compound is inferior to x, the new compound can be united to oxygen, to chlorine, to iodine, &c.; if it is also susceptible of separating intact from these combinations under the influence of agents endowed with preponderating affinities for these simple bodies, it will behave as a true radical, being able to absorb a greater number of atoms of oxygen or of chlorine in proportion as the number of equivalents of ethyl which it may contain shall be smaller. Experience teaches in like manner that, in proportion as the number of equivalents of the alcoholic radical which unites with A goes on increasing, the resulting compound is endowed with affinities for oxygen, chlorine, &c., more and more energetic, the oxygenated compounds, however acid or neutral they were primitively, advancing towards alkalinity in the most decided manner.

Arsenic presents us in this respect a most striking and instructive example. This body tends to form two principal groups,

$$AsX^3.$$

and $$AsX^5,$$

the last presenting the term of saturation.

We may then form with arsenic and methyl at a maximum five definite compounds, the last being incapable of producing new compounds, because it is at saturation. Now, the experiments of Bunsen, of Landolt, of Baeyer and my own, demonstrate that we may form with arsenic and methyl the four compounds

$$AsMe,\ AsMe,^2\ AsMe^3,\ AsMe^4.$$

If we place these different compounds in presence of an excess of oxygen so as to obtain compounds at saturation we shall have

$$AsMeO^4$$
$$AsMe^2O^3$$
$$AsMe^3O^2$$
$$AsMe^4O,$$

which form with water the following compounds:

$AsMeO^4 2HO$ bibasic acid,
$AsMe^2O^3HO$ monobasic acid,
$AsMe^3O^2$ indifferent body,
$AsMe^4O,HO$ powerful base, comparable to potassa and soda.

The oxygenated compound which forms the superior term presenting the characters of a very energetic acid, we see that the last possesses such alkalinity that it may rival the most powerful bases.

Azote [nitrogen,] like arsenic, is susceptible of giving origin to five perfectly definite groups which may be formulized in the following manner:

$$AzX$$
$$AzX^2$$
$$AzX^3$$
$$AzX^4$$
$$AzX^5$$

These five groups which are of the greatest interest may be realized with oxygen. We are also acquainted with compounds containing both oxygen and other elements, such as chloronitrous and chloronitric acids which may be obtained by the direct union of chlorine with binoxide of azote [nitrogen] compounds which correspond to nitrous and hyponitric acids.

Contrary to what is observed with oxygen we have been able to isolate but a single definite hydrogenated compound of azote [nitrogen.]

This compound, which is ammonia

$$AzH^3$$

corresponds to the group

$$AzX^3$$

We have previously seen how we may, starting from this product, produce the most diverse compounds by a series of regular substitutions. Ammonia, being endowed with basic properties, will beget bases by these substitutions, if we replace a part or all of its hydrogen by bodies whose chemical functions are analogous, while it will yield neutral bodies and even acids if we replace this hydrogen by bodies whose chemical functions are opposite.

Substitute, for example, in place of the hydrogen any one of the radicals of the divers alcoholic series, phenyl or one of its homologues, &c., we obtain products which present not only the most complete parallelism of composition, but whose chemical characters are so confounded with those of ammonia, that the history of these various compounds is deduced from that of the substance itself. This result is easily explained when we reflect that the chemical functions of these carburets of hydrogen much resemble those of hydrogen; but what is very worthy of attention is that the alkalinity of these compounds increases with the number of equivalents of methyl, of ethyl, &c., which have been substituted. This observation becomes more striking still when we consider the compounds resulting from similar substitutions effected in phosphuretted hydrogen.

PhH^3

The trimethylphosphine $PhMe^3$
and the triethylphosphine PhE^3,

which differ as we see from this gas only by the substitution of 3 equivalents of methyl or of ethyl for 3 equivalents of hydrogen, possess the property of combining with different acids, but this is not the case with phosphuretted hydrogen which unites only with iodohydric acid, a compound so unstable that the slightest influences are sufficient for its destruction.

If we have been unable up to this time to form of nitrogen and hydrogen, a compound corresponding to the maximum of saturation,

$$AzX^5$$

we nevertheless know a great many which may be considered as belonging to this type, which are comprised in the general formula.

$$Az\ (H^4X).$$

It is thus that dry ammoniacal gas, like a great number of carburets of hydrogen, directly unites, volume to volume, with chlorohydric, bromohydric, iodohydric, cyanhydric; etc., gases, to form compounds which enter in the preceding formula and which may be expressed by the symbols

$$(Az\ (H^4Cl)\ (Az\ (H^4Br)\ (Az\ (H^4I)\ (Az\ (H^4Cy),\ \text{etc.}$$

(~~To be continued~~.)

Some chemists, with Ampere, admit into these compounds the existence of the radical

$$AzH^4,$$

designated under the name of ammonium, [NH^4] a radical which has not yet been isolated notwithstanding all the efforts which have been made, and, it would be at a risk of being illogical, to admit its formation by contact of chlorohydric acid with ammonia, the tendency of the latter to unite with hydrogen being so feeble as not to be sufficient to overcome the powerful affinity of chlorine for this gas. We know that when we cause the amalgam of potassium to act on a concentrated solution of an ammoniacal salt, with the view of obtaining the amalgam in which is admitted the existence of the compound

$$AzH^4$$

this is spontaneously destroyed, although its union with mercury tends to give it stability. It cannot be supposed more reasonably, that the affinity of chlorine for the compound, which tends to be produced, may be susceptible of determining its formation; for it is enough to cause chlorine to act on a solution of chlorohydrate of ammonia, by aid of a gentle heat, to see the compound resolve itself entirely into azote [nitrogen], which is disengaged in a gaseous form, and chlorohydric acid which remains dissolved. Is it then not more simple and more logical to admit that the union of two bodies placed in contact, begets a particular group which is referred to the type

$$AzX^5,$$

which appears to be the term of saturation of the compounds which azote [nitrogen] is susceptible of forming?

The same is true in regard to the derivatives from ammonia known under the name of trimethyliac, triethyliac, triamyliac, &c., which are formed, as we know, by the substitution of three molecules of methyl, ethyl, or amyl, for the three molecules of hydrogen which it contains; these compounds which may be represented by the symbols

$$AzMe^3 \quad AzE^3 \quad Az\,Amy^3$$

may fix either

$$HCl \text{ or its analogues}$$

or $MeCl \quad ECl \quad AmyCl$

to form compounds of the same order,

$$Az\,(Me^4Cl)\;Az\;(E^4Cl)$$

in which we must admit, without more serious reasons, the existence of new radicals derived from ammonium, radicals which it has been as impossible up to this time to isolate as ammonium itself. There is certainly nothing improbable in supposing that we may obtain a compound formed of one equivalent of azote and four equivalents of hydrogen, but the mind refuses to admit that a like compound can arise from the contact of chlorohydric, bromohydric acids, &c., while we know the considerable affinity which the constituent principles of these gases have for each other, and the enormous resistance they offer to decomposition. Is it not much more simple to admit that azote as well as its congeners is susceptible of forming divers combinations of which the term of saturation is of the form

$$RX^5.$$

As long as this limit is not obtained, we may add to the product under consideration, one or more equivalents of the same substance or of different substances, until we have reached it. The inferior term which is considered to play the part of fixing certain bodies to form definite compounds, could it be separated intact from these compounds by the intervention of reagents or forces purely physical, would present the properties which characterize simple bodies.

There is certainly between the ammoniacal compounds and those which the alkaline metals form, analogies well worthy of serious study; but it must, however, be confessed, they are found more in the form than in the substance, which does not constitute a sufficient reason for assimilating them with each other.

Proceeding from azote towards arsenic we observe in corresponding compounds quite curious differences, on which I desire in a few words to fix your attention.

Ammonia, in exchanging all its hydrogen for the groups methyl, ethyl, propyl, amyl, &c., gives rise to the compounds

$$AzMe^3\;AzE^3\;AzPr^3\;Az\,Amy^3,$$

which may slightly enter into the formula which constitutes the term of saturation by the fixation of a molecule of chlorohydric, bromohydric acid, &c., after the manner of ammonia, but which are incapable of uniting with two molecules of oxygen, of chlorine, or of sulphur, to form analogous compounds, which shows that these products are wanting in the characters of radicals.

The corresponding compounds

$$PhMe^3\ PhE^3,\ \&c.,$$

like the preceding, have the property of uniting with acids, and also of fixing $O^2Cl^2S^2$, in the manner of simple bodies.

Their analogues of the arsenic series,

$$AsMe^3\ AsE^3\ \&c.,$$

incapable of uniting with acids, fix with the greatest facility $O^2Cl^2S^2$, &c. So that phosphorus serves in some way as the transition between the compounds of nitrogen and the corresponding products formed by arsenic.

We have seen above, that among simple bodies there is a certain number which are susceptible of forming with methyl, ethyl, &c., compounds corresponding to oxides, chlorides, &c., in which oxygen or chlorine would be replaced by equivalent quantities of preceding groups. The numerous researches undertaken by M. Frankland with the view of isolating the alcoholic radicals have made us acquainted with two very remarkable compounds—the methyluret and ethyluret of zinc, belonging to the group

$$ZnX,$$

which have become a source of reactions full of interest. The most recent labors of M. Vanklyn in like manner have taught us that the alkaline metals may form analogous compounds; only these latter are so unstable, that, up to the present time, we have been unable to separate them from the compound which they form with the methyluret or ethyluret of zinc.

Left in contact with oxygen, these products absorb this gas with great avidity. The latter, far from uniting with the ternary group, brings complete destruction to the molecule by burning the elements which compose it; hence the inflammation of the substance. In presence of water these liquids induce its immediate decomposition, producing metallic oxides, and hydride of methyl or of ethyl, a result easy to understand if we reflect that these different products represent compounds at saturation, containing elements endowed with energetic affinities for the constituent principles of this liquid, and consequently very apt to cause its destruction in decomposing themselves. The ethyluret of zinc, no more than the alkaline ethylurets, can act as a simple body, since it represents the most stable group which these metals are capable of forming, and consequently the name of *organo-metallic* radicals, by which they have been designated, is entirely inexact.

When we replace the zinc by the metals of diverse sections, we obtain in some cases entirely analogous reactions.

Under certain circumstances free ethylurets are formed, as in the case of magnesium; in others, and especially with tin, we obtain perfectly definite iodides.

A close examination of these interesting products, the study of their metamorphoses, and the circumstances of their production, have led me to consider all those which act in the manner of simple bodies, as not having attained the limit of saturation. This I propose to demonstrate to you now, abandoning the domain of hypotheses to enter into that of facts.

Magnesium, like zinc, which it resembles in so many respects, appearing susceptible of forming but a single group of the form

$$MgX,$$

should evidently form by its union with methyl and ethyl only one combination. Experiment fully realized my expectatoins.

When filings of magnesium are placed in contact with the iodides of ethyl or methyl, a quite vivid reaction is manifested, and the mixture becomes strongly heated. If, after having mastered it by affusions of cold water, we introduce it into tubes sealed by a lamp, then maintain it during several hours between 120° and 130° [centigrade], we finally obtain a white mass which is resolved by distillation into several products. In effecting this operation in an atmosphere of hydrogen, we collect in the recipient a mixture of iodide of ethyl or of methyl, and a very volatile liquid possessing an aliaceous odor, which takes fire in the air, and with violence decomposes water upon which it may be projected; the residue consists of iodide of magnesium. A new rectification made on the raw product permits the separation of the inflammable liquid from the iodides of methyl or of ethyl unaltered.

Analysis of these products, their manner of acting in respect to free oxygen and water, their manifest analogies to the zinc methyl and the zinc ethyl, leads us to represent them by the formulæ

$$Mg\ (C^2H^3) \text{ and } Mg\ (C^4H^5).$$

In the reciprocal action of magnesium and the iodides of ethyl and of methyl, there is produced an abundance of gases which, in the case of the ethylic compound, consist of

$$C^8H^{10}\ C^4H^4 \text{ and } C^4H^6.$$

With the iodide of methyl we obtain the products

$$C^4H^6 \text{ and } C^2H^4.$$

The action of magnesium upon the iodides of ethyl and of methyl is entirely comparable to that which zinc exercises upon these compounds.

The ethylurets and methylurets which arise in this contact, correspond to the group

$$MgX,$$

the only stable one which magnesium can form. We conceive therefore that these compounds, like the ethylurets and methylurets of zinc, are incapable of forming new combinations by assimilating one or several molecules of certain simple bodies, the latter being able only to induce the destruction of these compounds, to give rise to new groups which possess a more stable equilibrium.

Aluminium while cold exerts no action upon the iodide of ethyl; at 100° [centigrade], the attack is very manifest; in maintaining the mixture during twenty-four hours at 130° in hermetically sealed tubes, the reaction is complete. If the ethylic iodide be used in slight excess, the metal entirely disappears, and we find in the tubes a thick, brownish liquid, which gives off to the air abundant fumes. In distilling the contents of the tubes in an apparatus filled with hydrogen, we collect in the recipient a light amber-colored liquid, the disagreeable and penetrating odor of which recalls that of altered turpentine. This liquid fumes strongly in the air, and inflames when projected into an atmosphere of oxygen or chlorine, disengaging violet vapors. It decomposes water in a sudden manner with a true explosion, producing alumina and iodohydric acid; it disengages at the same time an inflammable gas which burns with a pale blue flame.

This compound, which boils at about 350°, contains both aluminium and iodine, as well as carbon and hydrogen, in the proportions which constitute ethyl.

Numerous analyses of this product, and the decomposition which it undergoes with water, lead to the following formula:

$$C^{12}H^{15}\,Al^{4}\,I^{3} = Al^{2}\,I^{3},\,Al^{2}\,(C^{4}H^{5})^{3},$$

which would make of it a compound of one equivalent of the iodide of aluminium with the corresponding ethyluret.

The zinc ethyl attacks it briskly, producing a very inflammable volatile liquid, which appears to be aluminethyl.

The iodide of methyl behaves towards aluminium in the same manner as the iodide of ethyl. As in the preceding case, we obtain a volatile liquid at a high temperature, burning in the air, and decomposing water suddenly, giving rise to hydruret of methyl (gas of marshes). The composition of this product, which contains at once aluminium, iodine and the elements of methyl, may be represented by the formula

$$C^{6}H^{3}Al^{4}1^{3} = Al^{2}I^{3},Al^{2}(C^{2}H^{3})^{3}.$$

Glucinium strongly attacks iodide of ethyl when heated with this liquid in hermetically sealed tubes. We then obtain, as with magnesium, a solid product, which distillation separates into iodide of glucinium, and an odorous volatile liquid possessing the property of decomposing water suddenly after the manner of the preceding substances, disengaging an inflammable gas. The behaviour of this liquid towards water seems to indicate that it is of a nature analogous to that of the compounds furnished by magnesium and aluminium. The very small quantity of glucinium at my disposal did not permit me to establish its constitution by analysis.

Iron attacks iodide of ethyl briskly, at about 175° to 180° [centigrade]; gases are produced abundantly, and we obtain an iodide of iron, but I have not been able to obtain in this reaction any definite ethyl compound.

Chrome even at 200° does not appear to react in any manner upon iodide of ethyl. It is the same with molybdenum and titanium.

Metallic tin in the form of leaves is rapidly attacked by iodohydric ether, when we maintain these bodies enclosed in hermetically sealed tubes during several hours at a temperature of from 140° to 150°. The reaction is effected even in a bath of boiling water, but in this case a much longer time is required. It is also effected at an ordinary temperature, as was ascertained by M. Frankland, by the intervention of solar radiation.

If care is taken to employ from two to two and a half parts by weight of the iodide of ethyl for one part of tin, the metal disappears entirely, and if the substances are pure and very dry, the tubes contain a solid white mass formed of long intercrossed needles which are soiled by a small quantity of yellow or brownish oil which colors them. When we break the point of the tubes, most commonly there is no trace of gas disengaged. The crystals are easily purified by drying, compressing them between folds of bibulous paper, dissolving them in alcohol and abandoning the liquor to spontaneous evaporation. Finally, we obtain after one or two crystallizations fine colorless prisms, having considerable lustre and entirely free from odor. The oil which soils the crystals, whose pungent, insupportable odor recalls that of horseradish and mustard, is a mixture of the iodide of ethyl which has taken no part in the reaction with the iodide of a ternary compound containing carbon, hydrogen and tin. Under some circumstances we find in the tubes also a small quantity of a red crystalline powder which is iodide of tin.

The prismatic crystals brought to a state of purity, melt at 42° into a very limpid colorless liquid, which usually boils between 245° and 246°, and distils without alteration.

Alcohol dissolves them in large proportion, particularly when hot.

Ether readily dissolves them even when cold.

Little soluble in cold water, they are dissolved in notable proportion when at the boiling temperature.

Rectified wood spirit dissolves them like alcohol.

An alcoholic solution of these crystals is immediately decomposed by sulphate, nitrate, acetate, and butyrate of silver, forming insoluble iodide of silver and corresponding salts which crystallize readily by the evaporation of alcoholic distillation.

Analysis of these crystals leads to the formula

$$SnC^4H^5I.$$

The behaviour of this product with reagents leads us to regard it as an iodide of a ternary compound formed of one molecule of tin and a molecule of ethyl, or as corresponding with the group.

$$SnX^2,$$

which represents the limit of saturation of the compounds of tin.

Their very simple formation is explained by means of the equation

$$Sn+C^4H^5I=SnC^4H^5I.$$

In considering the group

$$SnC^4H^5$$

as a radical, the preceding compound would become an iodide entirely comparable to metallic iodides, the radical moreover being susceptible of separation from the combination by the intervention of metals more electro-positive than tin.

The caustic alkalis, potassa, soda, ammonia, cause in a solution of the preceding compound a white, flocculent, amorphous precipitate, insoluble in an excess of these reagents. This product, which does not differ from the preceding, except that the molecule of iodine is replaced by a molecule of oxygen, would be an oxide of this radical, which we will designate under the name of *stannethyl;* henceforward we shall represent its composition by the formula

$$SnC^4H^5O.$$

This compound unites directly with acids, saturates the most energetic, and forms salts which, whenever they are soluble, crystallize with the greatest ease. Their composition is expressed by the general formula

$$A,SnC^4H^5O.$$

The hydracids behave with it as with metallic oxides, the hydrogen seizing upon its oxygen to form water, while the radical of the hydracid goes to the stannethyl group to form a definite compound,

$$SnC^4H^5O+RH=HO+SnC^4H^5R.$$

We obtain in this way the chloride and bromide of stannethyl,

$$SnC^4H^5Cl$$

$$SnC^4H^5Br,$$

compounds which crystallize in magnificent colorless prisms, isomorphous with the iodide.

The oil with the odor of mustard, which is formed in quantities scarcely appreciable when we make use of pure tin, may be obtained in considerable proportions, if we substitute alloys containing from 8 to 12 per cent. of sodium, taking care to interpose besides an excess of iodohydric ether. When the alloy contains but from 4 to 5 per cent. of the alkaline metal, there is formed simultaneously the solid and crystallizable iodide, as well as the strongly smelling liquid compound. With alloys of from 10 to 12 per cent. the latter is formed almost exclusively.

The formation of this product, to which analysis assigns the formula

$$Sn^2(C^4H^5)^3I,$$

may be explained by means of the equation

$$Sn^2Na^2+3(C^4H^5I)=Sn^2(C^4H^5)^3I+2NaI.$$

This liquid compound, abandoning its iodine to the salts of silver to form crystallizable and perfectly definite products, may be, as well as the solid iodide, considered as the iodide of a new radical which we shall designate under the name of *sesquistannethyl.*

A dilute solution of potassa or of soda, occasions no precipitate in the solution of this product; introduced into a distillatory vessel with a concentrated ley of potassa, or better, with fragments of hydrated potassa slightly moistened, and the mixture warmed, we immediately see condensed in the recipient with aqueous vapor a heavy oily matter, which, on cooling, concretes into a colorless mass formed of inter-crossed prisms.

This substance, which crystallizes readily, and whose pungent odor recalls, although in a less degree, that of the oily iodide, is nothing but the hydrate of an oxide corresponding to this iodide, the composition of which may be expressed perhaps by the formula

$$Sn^2(C^4H^5)^3O,HO.$$

Distilled upon anhydrous barytes, it abandons its equivalent of water to yield a limpid volatile oil, which is the anhydrous oxide.

If water is added drop by drop to this oil, the mixture heats and immediately concretes, producing the crystallized hydrate.

This oxide, which turns the syrup of violets green, and restores to blue red tournesol paper, after the manner of alkalies, saturates the strongest acids, and forms salts, for the most part soluble, which readily crystallize, and furnish specimens of great beauty. These salts, which are generally volatile, and, when heated, yield an odor analogous to that of the free base, are represented by the general formula

$$A,Sn^2(C^4H^5)^3O.$$

The hydracids behave towards the oxide in the same manner as towards oxygen bases, giving rise to water and to compounds which differ from this oxide only in the substitution of the radical of the hydracid for oxygen,

$$Sn^2(C^4H^5)^3O+RH=HO+Sn^2(C^4H^5)^3R.$$

The chloride and bromide are liquids like the iodide, and are concreted by a slight reduction of temperature, and yield a still more insupportable odor.

The oily iodide unites directly with ammonia, and forms a combination perfectly definite, which can be obtained in the form of magnificent prisms, by introducing into a tube, and hermetically sealing it, a mixture of the liquid iodide and ammonia dissolved in alcohol. The tube, heated in a water bath, deposits on cooling long prisms, the composition of which is represented by the formula

$$Sn^2(C^4H^5)^3I, 2AzH^3.$$

If we cause the iodide of ethyl to act on alloys of tin and sodium, strongly charged with the alkaline metal, and are careful to use the alloy in excess, a very brisk reaction is manifested, and, in this case, instead of having combinations of the metal with ethyl and iodine, we obtain only ethylurets.

In the reciprocal action of these bodies, we obtain three distinct compounds, namely:

1st. A thick liquid decomposable by heat

$$Sn(C^4H^5),$$

which is *stannethyl;*

2d. A very mobile volatile liquid, boiling between 240° and 250° [C.],

$$Sn^2(C^4H^5)^3,$$

which I name *sesquistannethyl;*

3d. A very mobile, very volatile liquid, boiling between 175° and 180°, which is formed only in very small quantity,

$$Sn(C^4H^5)^2,$$

is the *distannethyl*, which Messrs. Buckton and Frankland each obtained from the reciprocal action of zinc, ethyl and iodide of stannethyl,

$$Sn(C^4H^5)I+ZnC^4H^5=Sn(C^4H^5)^2+ZnI.$$

If we cause the iodide to act on the viscid liquid, we produce crystallized iodide; the action of the same body upon the sesquistannethyl cold, gives rise immediately to the formation of the oily iodide with the mustard odor; distannethyl cold produces nothing by contact with iodine. Warmed, on the contrary, a brisk reaction is manifested, and is immediately perceived by the discoloration of the liquid, the iodine being substituted in equivalent proportions, and in proportion to the quantity of iodine and to the duration of the contact, we may obtain at pleasure either the oily iodide, the crystallized iodide, or the iodide of tin.

While stannethyl and sesquistannethyl are susceptible of union directly with oxygen, chlorine and iodine, to form compounds which enter into the group

$$SnX^2,$$

and to be eliminated from their combinations under the influence of preponderating affinities, simulate the properties of simple bodies and behave like true radicals, the distannethyl, which represents the limit of saturation, is entirely incapable of forming compounds, and can only exchange a portion of its elements to assimilate others in equivalent proportion, always preserving the integrity of its group.

We may readily pass back from the series of sesquistannethyl that of stannethyl, and reciprocally by aid of reactions which are easiest of execution. Thus by the action of iodine upon the iodide of sesquistannethyl we produce the iodide of stannethyl, with the formation of iodohydric ether,

$$Sn^2(C^4H^5)^3I+2\,I=C^4H^5I+2(SnC^4H^5I),$$

while by distilling the oxide of stannethyl with caustic potassa, we obtain the oxide of sesquistannethyl, with separation of a part of the tin under the form of stannic acid,

$$3(SnC^4H^5O)+KO=SnO^2KO+Sn^2(C^4H^5)^3O.$$

The experiments of which I have just related a succinct summary, very clearly establish, that in the reciprocal action with iodide of ethyl and of tin, compounds are formed which all belong to the group

$$SnX^2.$$

It was important to determine the mechanical constitution of these products, and to fix their true equivalent.

Among the compounds of tin which belong to the preceding group we will cite the bichloride

$$SnCl^2.$$

Now, the determination of the density of vapor of this product by M. Dumas, demonstrating that this formula represents two volumes, it will be proper to double it, in order to make it harmonize with the best defined compounds. It will be the same with its analogue

$$SnE^2,$$

which, according to the experiments of M. Frankland, will likewise correspond to two volumes of vapor.

The chlorides of stannethyl and sesquistannethyl being susceptible of distillation without alteration, like the bichloride of tin, it at once becomes hence interesting to determine the density of these products in their gaseous form. Experiment teaches us that while the formula

$$Sn\,C^4\,H^5\,Cl.$$

corresponds to two volumes, that which represents the chloride of sesquistannethyl

$$Sn^2\,(C^4\,H^5)^3\,Cl$$

corresponds to four volumes, a constitution which should be very different, although referrible to the same group.

If we replace the iodohydric ether by the iodide of methyl, we obtain a series of products, analogous to those whose history we have just sketched. If we employ pure tin, we have formed, in considerable proportion, a solid iodide, crystallizing in beautiful sulphur-yellow crystals, melting at 30° [C.] into a limpid liquid which boils regularly at a temperature of 228°, and whose composition is represented by the formula

$$Sn\,C^2\,H^3\,I.$$

Besides this crystallizable iodide, there is found, though in much smaller proportion, a liquid iodide a little more volatile than the preceding, having an insupportable odor, the composition of which, analogous to that of the iodide of sesquistannethyl, is represented by the formula

$$Sn^2\,(C^2\,H^3)^3\,I,$$

is the iodide of sesquistannethyl.

If we replace the pure tin by an alloy of this metal with sodium, taking care to employ the iodide of methyl in excess, we observe precisely the inverse, as in the case of the ethylic iodide; that is, while we obtain liquid iodide in considerable proportions, we procure but very small quantities of solid iodide.

When the solution of solid iodide is treated by alkaline liquids, there is separated a flocculent white precipitate insoluble in an excess of the reagent, the composition of which, represented by the formula

$$Sn\,(C^2\,H^3)\,O,$$

teaches us that it is the oxide of sesquistanmethyl, while the oily iodide, distilled from fragments of caustic potassa, disengages irritating vapors which are condensed in the recipient under the form of a heavy oil, which is not slow in being converted into beautiful prisms. This product, the composition of which is represented by the formula

$$Sn^2\,(C^2\,H^3)^3\,O,$$

is simply the hydrated oxide of sesquistanmethyl which presents the most perfect isomorphism with the corresponding ethylic compound. Like its homologue, it is separated by distillation on caustic barytes into anhydrous oxide and water.

The oxides of stanmethyl and of sesquistanmethyl saturate the most energetic acids, and form compounds which, crystallizing for the most part in a remarkable manner, possess properties analogous to those of ethylic combinations, and are entirely isomorphous with them.

The hydracids behave the same, and form products entirely similar.

The determination of the density of the chlorides of stannethyl and of sesquistanmethyl, under the gaseous form, lead to conclusions, identical to those which the chlorides of stannethyl and of sesquistanmethyl furnish. It is thus that

$Sn\,C^2\,H^3\,Cl$ represents 2 vol. of vapor,
while $Sn^2\,(C^2\,H^3)^3\,Cl$ represents 4 vol. of vapor.

Now if we consider that the molecule of all volatile bodies, whose equivalent can be accurately established by chemical means, always correspond to four volumes of vapor, it will be proper to double all the formulæ of the compounds of stannethyl and of stanmethyl. Consequently we should formulate these different compounds in the following manner:

$Sn^2 E^4 = 4$ vol. vapor.	Tetrastannethyl
$Sn^2 E^3 Cl =$	Chloride of tristannethyl
$Sn^2 E^2 Cl^2 =$	Chloride of distannethyl.
$Sn^2 E Cl^3 =$	"
$Sn^2 Cl^4 =$	Tetrachloride of tin ;

all these different compounds belonging to the same type.

Now the filiation which we here indicate is not purely imaginary, and the behaviour of iodine in respect to the compound

$$Sn^2 E^4 = 4 \text{ vol. vap.}$$

demonstrates it in the most evident manner. Indeed, if this product in excess relatively to iodine, avoiding too great elevation of temperature, an equivalent of ethyl is eliminated in the form of iodide, while there appears at the same time this oil, whose insupportable odor recalls that of mustard, and which we have denominated iodide of sesquistannethyl; if we double the proportion of iodine and favor the reaction by the aid of heat, instead of endeavoring to moderate it by affusions of cold water, there is a separation of a second molecule of ethyl in the state of iodine, and formation of the beautiful crystallized matter to which we have given the name of iodide of stannethyl. If we use an excess of iodine, all the ethyl separates from the state of iodide, and we finally obtain the red iodide of tin. Such is the result which we obtain by warming in close vessels an excess of iodine either with tetrastannethyl, or with the iodides of sesquistannethyl and of stannethyl. From the tetrastannethyl we pass to the corresponding iodide by the simple phenomena of substitution.

The action of acids on tetrastannethyl leads to exactly similar conclusions. If we introduce into a tube a mixture of chlorohydric acid and tetrastannethyl, we observe no reaction, and even after contact of some hours at the ordinary temperature, we may withdraw from the mixture both substances perfectly intact. If these two substances are placed in a hermetically sealed tube and then heated, the tetrastannethyl is modified to an extent proportioned to the duration of the contact. At first we obtain an irritating oil which is the chloride of sesquistannethyl, this gives place afterwards to colorless crystals which analysis proves to be chloride of stannethyl, and by still more prolonged contact we finally obtain chloride of tin.

In these different phases there is developed a gas which is no other than hydruret of ethyl; these very simple reactions, which besides agree perfectly with the preceding, may be expressed by means of the following equations:

$$Sn^2 (C^4 H^5)^4 + H\,Cl = Sn^2 (C^4 H^5)^3\,Cl + C^4 H^5 H$$

$$Sn^2 (C^4 H^5)^4 + 2H\,Cl = Sn^2 (C^4 H^5)^2\,Cl^2 + 2C^4 H^5 H$$

$$Sn^2 (C^4 H^5)^4 + 4H\,Cl = Sn^2\,Cl^4 + 4C^4 H^5 H.$$

And the manner in which the iodides of sesquistannethyl and of stannethyl behave with the zinc ethyl, seems to me to completely confirm this hypothesis.

We know from the precise labors of Messrs. Frankland and Buckton that in causing the iodide of stannethyl to act upon zinc ethyl, we obtain iodide of zinc and of distannethyl, and it is precisely this reaction which led them to the discovery of this compound. And so, too, in causing the iodide of stanmethyl to act on zinc methyl, we produce distanmethyl. Indeed, we have

$$Sn\,(C^4H^5)\,I + Zn\,C^4H^5 = Zn\,I + Sn\,(C^4H^5)^2$$

$$Sn\,(C^2H^3)\,I + Zn\,C^2H^3 = Zn\,I + Sn\,(C^2H^3)^2$$

We would have likewise, according to these chemists:

$$Sn\,C^4H^5\,I + Zn\,C^2H^3 = Zn\,I + Sn\,(C^2H^3)\,(C^4H^5).$$

Now I have satisfied myself that bringing together zinc ethyl and the iodide of sesquistanmethyl, there is manifested a vivid reaction accompanied by the formation of an ethereal product perfectly analogous to distannethyl, the composition of which is expressed by the formula

$$Sn^2\,(C^2H^3)^3\,(C^4H^5) = 4\text{ vol.}$$

This necessarily indicates the group

$$Sn^2X^4$$

as the point of departure of these different products, which we may consider as being derived from it, by partial substitutions or by a complete substitution. The tin hence becomes a simple tetratomic radical.

Tin in its contact with the iodides of ethyl and of methyl begets, as we see, a series of products, all possessed of a simple constitution, which are referable to the preceding group. As long as the molecules of methyl or of ethyl which are joined with the tin do not exceed four, that is, as long as saturation is not satisfied, the compounds thus formed may assimilate one or two molecules of oxygen, of chlorine, acting in the manner of *true* radicals. This limit attained, the obtained product possesses, as far as relates to combination, the most absolute neutrality. These results establish, I think, quite clearly, that a body, though a compound, will always play the part of a radical, whenever, being below the limit of saturation, it is endowed with such stability that the equilibrium of its group may not be broken, either by the affinity of simple bodies with which it is put in contact, for the elements which enter into its constitution, or under the influence of forces to which it may be subjected to separate it from combinations of which it forms a part.

The iodides of distannethyl and of tristannethyl, of distanmethyl and of tristanmethyl unite with ammonia after the manner of biniodide of tin, giving rise to compounds very clearly crystallized; those which result from the union of the iodides of tristannethyl and tristanmethyl affect the form of prisms which acquire quite a large volume when we replace the dry alcoholic gas by an alcoholic solution. Aniline, toluidine, cumidine, &c. give similar results, yielding very beautiful products with ammonia.

Lead, like tin, forms with ethyl and methyl clearly defined compounds: *Plumbodiethyl*

$$Pb\,(C^4H^5)^2$$

may be obtained by causing the iodide of ethyl to act upon alloys of lead and sodium, rich in alkaline metal, as M. Lœwig ascertained, or by the reciprocal action of chloride of lead and of zinc ethyl, a much more simple method employed by Messrs. Frankland and Buckton. We do not obtain in this case ethyluret of lead corresponding to the protoxide; there is separation of one-half of the metal and production of a compound which corresponds to the puce-colored [gray] oxide.

The reaction is easily explained by means of the equation.

$$2Pb\,Cl + 2(C^4H^5Zn) = 2Zn\,Cl + Pb\,(C^4H^5)^2.$$

Plumbodiethyl representing the limit of saturation of the compounds which lead forms, we are not surprised to learn that this product like tetrastannethyl, is incapable of uniting with oxygen, chlorine, iodine, &c.

If we warm this liquid with a concentrated solution of chlorohydric gas, an inflammable gas is disengaged, and on cooling we see deposited beautiful satinny needles, the composition of which is represented by the formula

$$Pb^2\,(C^4H^5)^3\,Cl.$$

The reaction which gives rise to this product may be expressed by the equation

$$2(Pb\,(C^4H^5)^2) + H\,Cl = C^4H^5H + Pb^2\,(C^4H^5)^3\,Cl.$$

Iodine gives with plumbodiethyl an analogous product represented by the formula

$$Pb^2\,(C^4H^5)^3\,I.$$

Iodide of ethyl is separated at the same time.

When we employ an excess of iodine we obtain iodide of ethyl and iodide of lead.

I am satisfied for my part that in replacing zinc ethyl by zinc methyl we obtain plumbodimethyl which is formed in like manner by causing the iodide of methyl to act upon an alloy formed of five parts of lead with one of sodium ; but the first method is much preferable.

In this way we obtain a very mobile and colorless liquid whose strong and peculiar odor reminds us of camphor and mouldiness. Incapable of uniting either with oxygen or chlorine or iodine, this compound separates in the manner of its ethylated homologue. Similar results are observed when we employ chlorohydric or sulphuric acids,

$$2(Pb\,(C^2H^3)^2) + H\,Cl = C^2H^3\,H + Pb^2\,(C^2H^3)^3\,Cl.$$

I merely mention the ethylated and methylated compounds of mercury which Messrs. Frankland, Strecker and Buckton have so completely studied.

A profound examination of these compounds would lead us to conclusions entirely similar to those which we have deduced from the study of the preceding combinations.

Not to consume more of your time, and to demonstrate to you by a last illustration still more conclusive than the preceding, that bodies which act as radicals are complex substances in which saturation is not satisfied, I am about to submit a summary description of the ethylate and methylate compounds formed by bodies of the family of azote, or nitrogen, which will afford us results of the highest interest.

The different simple bodies which constitute this family have a great tendency to form the two groups

$$RX^3$$

and

$$RX^5.$$

Ammonia belongs to the first group, as well as the gases designated under the names phosphuretted, arseniuretted, antimoniuretted hydrogen. But if these compounds are represented by parallel formulæ, it must be admitted that we do not observe much analogy in their chemical actions; thus, while ammonia unites directly with the strongest acids, and saturates them completely, phosphuretted hydrogen combines only with some acids, and forms very unstable compounds, and the corresponding compounds of arsenic and antimony are entirely incapable of forming saline compounds. But if in those hydrogen compounds we replace all the hydrogen by equivalent proportions of ethyl or of methyl, we obtain the products

$$Az\,E^3 \qquad Ph\,E^3 \qquad As\,E^3 \qquad Sb\,E^3,$$

which present much more marked analogies.

The addition of a new equivalent of ethyl gives the products

$$Az\,E^4 \qquad Ph\,E^4 \qquad As\,E^4 \qquad Sb\,E^4,$$

which this time present such resemblances that the history of these different products is found to be based upon one of them.

The tendency which these different products have to fix an equivalent of oxygen, of chlorine, of iodine, &c. to beget compounds which enter into the group

$$RX^5,$$

is such that it is necessary to interpose quite energetic forces to destroy the equilibrium of these compounds; thus, the chlorides, bromides, iodides, &c.,

$$\begin{array}{llll} Az\,E^4\,Cl & Ph\,E^4\,Cl & As\,E^4\,Cl & Sb\,E^4\,Cl \\ Az\,E^4\,Br & Ph\,E^4\,Br & As\,E^4\,Br & Sb\,E^4\,Br \\ Az\,E^4\,I & Ph\,E^4\,I & As\,E^4\,I & Sb\,E^4\,I \end{array}$$

would not be decomposed by a boiling and concentrated ley of caustic potassa.

The corresponding oxides

$$\mathrm{Az\,E^4\,O} \qquad \mathrm{Ph\,E^4\,O} \qquad \mathrm{As\,E^4\,O} \qquad \mathrm{Sb\,E^4\,O}$$

all possess the most decided alkalinity, and in this respect rival potassa and soda. Like the latter, they restore to blue the reddened tincture of tournsol, disorganize the skin, saturate the most energetic acids, saponify fatty bodies, and behave like them towards metallic salts. Moreover, compounds formed by these oxides are isomorphous with corresponding compounds of potassium and sodium; it is the same with chlorides, iodides, &c. These analogies are so striking that the most prominent features presented in the history of alkaline metals may be followed in these compounds.

Among these curious compounds, even a very succinct analysis of which would carry me too far, I beg leave to select those referable to arsenic, which I have most especially studied; what I shall say of them may be applied, with slight modifications, to the others.

It is easy to demonstrate that arsenic placed in suitable conditions is susceptible of uniting successively with 1, 2, 3, 4 molecules of methyl to form compounds,

$$\mathrm{As\,Me}, \quad \mathrm{As\,Me^2}, \quad \mathrm{As\,Me^3}, \quad \mathrm{As\,Me^4},$$

which, not having attained the limit of saturation

$$\mathrm{As\,X^5},$$

are consequently susceptible of uniting with 4, 3, 2, 1, equivalents of oxygen, chlorine, iodine or sulphur, to finally yield compounds at saturation, the physiognomy of which will be very different. Thus if we consider the two extremes we shall have

$$\mathrm{As\,Me\,O^4} \;.\;.\;.\;.\;.\; \mathrm{As\,Me^4\,O}.$$

The first presenting the characters of an energetic acid, while the second offers us such analogy of properties with the alkaline bases that one might be tempted to confound it with potassa or soda.

These different combinations of methyl with arsenic are formed with the greatest facility in the reciprocal action of iodide of methyl and alkaline arseniurets. If we pour iodide of methyl, a little at a time, upon the arseniuret of potassium reduced to powder, and place it in a small globe previously filled with carbonic acid, we immediately perceive a very vivid action, which is manifested by a marked elevation of temperature. The moment this ceases to be produced we distill the mass in a current of inert gas, and collect a mixture of these products, namely:

1st. $As\ Me^2$ arsenidimethyl (cacodyl.)
2d. $As\ Me^3$ arsentrimethyl.
3d. $As\ Me^4\ I$, iodide of arsenimethylium.

The first term, which is nothing but the cacodyl of Bunsen, is easily obtained, as is known, by the distillation of a mixture of arsenious acid and acetate of potassa entirely deprived of water. We can produce the last in considerable proportion and in an immediate manner by causing iodide of methyl to act on cacodyl; we thus obtain, by crystallization in alcohol, cubes of great beauty, which possess the most perfect resemblance to those of iodide of potassium. The distillation of this substance from fragments of solid potassa yields the intermediate term in a state of entire purity, so that by means of acetate of potassa, iodide of methyl and arsenious acid, we can obtain the three products with the greatest facility.

Up to the present time I have been unable to obtain either the term at saturation $As\ Me^5$,
or the group

$$As\ Me^4,$$

the analogue of ammonium, the existence of which we may suppose in the crystallized iodide which we have called iodide of arsenmethylium. But the action of iodide upon the compound

$$As\ Me^4, I,$$

that of chlorine upon the corresponding compound

$$As\ Me^4, Cl,$$

will afford us the most instructive results, entirely analogous to those which result from the action of these bodies upon distanmethyl or the iodide of sesquistanmethyl, and while enabling us to comprehend the mechanism of the formation of products so varied, impart the most brilliant character of reality to the hypothesis which I announced at the commencement of this lecture on the constitution of organic radicles.

Potassium and sodium being susceptible of forming with iodide the compounds

$$KI \text{ and } KI^3,$$

we should expect to see the iodides

$$As\ E^4\ I \qquad Ph\ E^4\ I, \&c.$$

fix two new equivalents of iodine to form analogous compounds, which experiment proves in the most complete manner. Indeed, the researches of M. Veltzien have demonstrated to us the existence of the compounds

$AzMe^4 \quad I^3$
$AzE^4 \quad I^3$
$AzMe^3 E \quad I^3$
$AzMe E^3 \quad I^3$

Arsenic has furnished me results exactly similar; all these compounds crystallize in brown needles with metallic lustre, which remind us of the crystals of permanganate of potassa. They are generally slightly soluble in alcohol and in water: ether also dissolves them in slight proportion.

With arsenic I have realized the formation of the five following compounds, which are all isomorphous:

$AsMe^4 \quad I^3$
$AsE^4 \quad I^3$
$AsMe^3 E \quad I^3$
$AsMe E^3 \quad I^3$
$AsMe^2 E^2 \quad I^3$.

If it be now asked what action heat should exercise upon such compounds, the reply is easy. The affinity of iodine for methyl or ethyl should necessarily determine the separation of these products and bring us back inevitably to the group

AsX^3,

with elimination of a portion of the methyl or of the ethyl under the form of iodide.

Experiment confirms this in the clearest manner.

In submitting to distillation the compounds

$AsMe^4 \quad I^3$
and $AsE^4 \quad I^3$

I have obtained in the first case, the iodide of cacodyl, and in the second, iodide of arsendiethyl or ethylic cacodyl; the iodide of methyl or the iodide of ethyl is disengaged at the same time.

These reactions may be easily explained by means of the following equations:

$$AsMe^4 I^3 = 2Me\,I + AsMe^2 I$$
$$AsE^4 \; I^3 = 2E \; I + AsE^2 \; I.$$

Hence it is very probable that in causing two equivalents of iodine to act upon one equivalent of iodide of cacodyl, or three equivalents of iodine upon free cacodyl, so as to beget the tri-iodide, we would separate, under the influence of heat, one equivalent of methyl in the state of iodide, and at the same time would give rise to the iodide of arsenmonomethyl, which experiment fully confirms. Indeed, we have

$$AsMe^2 I + 2 I = Me I + AsMe I^2$$
$$AsMe^2 + 3 I = Me I + AsMe I^2,$$

compounds which both belong to the group

$$AsX^3.$$

If we distil the di-iodide of arsenmonomethyl with two equivalents of iodine, or cause five equivalents of iodine to react on the cacodyl, we obtain in the end iodide of methyl and iodide of arsenic

$$As I^3.$$

The ethylic compounds of arsenic have furnished me, as might be anticipated, results entirely comparable to the preceding. Indeed we have

$$As E^4 I^3 = 2 EI + As E^2 I$$
$$As E^2 I + I^2 = E I + As EI^2$$
$$As E I^2 + 2I = E I + As I^2$$

Starting from the ethylic or methylic compound of arsenic which forms the upper term, we then obtain, by the action of increasing proportions of iodine, a series of compounds which all belong to the most stable group

$$As X^3,$$

until, by a complete elimination of the alcoholic radical, we finally arrive at the iodide of arsenic, results which agree in such a striking manner with those presented by the ethyluret and methylurets of tin.

On the other hand we know, according to the admirable work of M. Baeyer, that when we cause chlorine in increasing quantity to act upon cacodyl, we obtain succcessively the products

$$AsMe^2 Cl,$$
$$AsMe^2 Cl^3;$$

which correspond to the groups

$$As X^3 \text{ and } As X^5.$$

The first, which is volatile without decomposition, is the monochloride of cacodyl; if we attempt to distil the second, the equilibrium is not slow to be broken, chloride of methyl is disengaged in the gaseous form, and we obtain a product of more simple composition, which itself soon distils, and which is nothing else than the bichloride of arsenmonomethyl. The reaction, which is very simple, is explained by means of the equation

$$\underset{\substack{\text{Trichloride of}\\ \text{Cacodyl}}}{\mathrm{As\,Me^2\,Cl^3}} = \underset{\substack{\text{Chloride of}\\ \text{Methyl}}}{\mathrm{Me\,Cl}} + \underset{\substack{\text{Bichloride of}\\ \text{Arsenmonomethyl.}}}{\mathrm{As\,Me\,Cl^2}}$$

The bichloride of arsenmonomethyl readily absorbs two new equivalents of chlorine, and yields a crystallized product corresponding to the group

$$\mathrm{As\,X^5}.$$

which is so unstable that gently warming it is sufficient to cause the separation of the last equivalent of chlorine, in the state of chloride at the same time that the arsenic passes to the condition of trichloride, in this way brought back to the group

$$\mathrm{As\,X^3},$$

which is the maximum of stability for the arsenic compounds.

I have satisfied myself that bromine, as analogies suggest, gives rise to perfectly similar results.

The clear reactions which the ethylic and methylic compounds of arsenic present, most strikingly confirm the views expressed by me at the commencement of this lecture, and which the study of the stannethyls had already clearly exposed, namely: that if bodies which act as radicals present, although complex, all the attributes of simple bodies playing sometimes the part of an electro-negative, and sometimes that of an electro-positive element, of supporter of combustion [comburant] or of combustible, it is that, on the one hand, they possess sufficient stability to enable us to engage them in combinations, and to return again, under the influence of certain forces, without destroying the equilibrium of their molecules, and on the other, the simple substances which compose them not having attained the term of saturation, tend to satisfy it when placed in suitable conditions.

Whenever then we establish contact between a compound formed by a simple body with methyl, or any one of its homologues corresponding to the condition of saturation, and the most electro negative bodies such as oxygen, chlorine, iodine,

&c., it is very evident that these will be incapable of adding to the group which we consider to form oxides, chlorides, iodides. We understand, on the contrary, that by a very simple phenomenon of double decomposition, we shall always be able to eliminate a part of the alcoholic radical in the form of oxide, chloride, &c., while an equivalent proportion of the simple body will take its place to form a product corresponding to the group which has served as the point of departure. Now the chlorine or iodine introduced in this way into the compound, being susceptible of exchanging with different simple bodies, notably with oxygen, the oxygenated compound being able to unite different acids after the manner of metallic oxides, and to form different salts, we readily explain how the residue ought to present all the appearances of a true elementary substance.