

THE TYPE THEORY

and the beginnings of VALENCE

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Class of 1900

B I B L I O G R A P H Y

Publications of those times

Wurtz - "Introduction to Chemical Philosophy" pp 1-154

Historics of Chemistry

Ernst von Neyer "History of Chemistry" pp 236-332

Tilden A Short History of the Progress of Scientific
Chemistry" pp 158 - 144

Venable "Short History of Chemistry" pp 114 - 139

Outline of Countents.

Introductory:

Older Radical Theory.

Basis in facts (Gay Lussac on Cyanogen
(Bunsen on Cacodyl comp.
(Liebig and Wohler on Benzoyl.

Attack on Dualism.

Basis in facts (Substitution
(Trichloracetic acid

Nucleus Theory of Laurent

Older Type Theory of Dumas

Type Theory

Gerhardts Theory of Residues

Basis (Work of Laurent and Gerhardt
(

Water Type - Laurent

Ammonia Type -- Wurtz

Hydrogen (Types -- Gerhardt -- Types of double decomposition.
and (Types of double decomposition.
Hydrochloric acid (Types of double decomposition.

Condensed Types -- Williamson

Mixed Types -- Odling

Discussion as to general merits of Type Theory.

Marsh gas Type -- Kekule

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The Type Idea and Beginning of the Theory of Valency.

Between the years 1820 and 1830, cases of isomerism multiplied so rapidly as to demand explanation. Berzelius said, "The isomerism of compounds in itself presupposes that the position of the atoms in them must be different." Later, attempts were made to group various organic compounds together upon the hypothetical basis of definite common radicals. The outgrowth of these attempts was the "Older Radical Theory" of Liebig and Berzelius.

The chief incentive to such labors was the research of Gay Lussac on cyanogen. He proved that cyanogen existed, unchanged, in various compounds, as well as in the free state.

Gay Lussac also held the view that ethylene was a common constituent of both alcohol and ether. Dumas and Boullay attempted to generalize this idea, to extend it to the derivatives of these substances. They assumed the existence of a radical, aetherin, $C_2 H_4$ ($H = 1$, $C = 6$, $O = 16$) in what we now call ethyl compounds. This "aetherin" was analogous to ammonia, being regarded as a base, capable of forming a hydrate with water, and "ethers" (or ethereal salts) with acids. The following table shows this view.

Etherin $C_2 H_4$

Alcohol $C_2 H_4 + H_2 O$

Ether $2 C_2 H_4 + H_2 O$

Hydrochloric ether $C_2 H_4 + HCl$

Acetic ether $2C_2 H_4 \quad C_8 H_6 O_3 \quad H_2 O$ Acetate of ammonium

$2NH_3 \quad C_8 H_6 O_3 \quad H_2 O$

This Etherin Theory was the fore runner of the Radical Theory only

so far as it tried to connect inorganic with organic chemistry.

Liebig and Wohler in '32 proved that a radical $C_{14}H_{10}O_2$ ($H = 1$, $C = 12$, $O = 16$) existed, unchanged, in numerous transformations of oil of bitter almonds and of Cl and Br compounds prepared from it. They showed, too, that this radical -- Benzoyl -- acted like an element in many compounds. Berzelius was so enthusiastic over this memorable research that for a time he abandoned his opposition to radicals containing oxygen. But within a year, he declared that radicals must have a biary structure, and that the idea of "oxygenated radicals" must be abandoned, as being out of concord with his electrochemical theory. Benzoyl was the oxide of $C_{14}H_{10}$. Ether, corresponding to inorganic bases, was suboxide of ethyl (C_2H_5)₂O

The work of Bunsen on the cacodyl compounds should be mentioned here. Bunsen proved that "alk-arsin," the product of distillation of acetate of potash with arsenious acid, contains the oxide of an arseniuretted radical $As_2 C_4 H_{12}$ ($H = 1$, $C = 12$, $As = 75$), this radical being isolable, and unchanged during a long series of reactions.

The main advantage from such labors was that it firmly fixed the analogy between organic and inorganic substances. Dumas, Liebig and Berzelius, differing on minor points, all agreed that compound radicals existed as distinct constituents in their compounds. Liebig, mainly because of Reguault's researches on "chloro-al-dehyde", gradually decided that radicals were alterable.

In 1837, Liebig and Dumas set forth their joint views in a paper, from which the following quotation is taken. "Organic chemistry possesses its own elements, which sometimes play the part of Cl or O, sometimes that of a metal. Leyanogen, amidogen, benzoyl, and the radicals of ammonia, of the fats, and of alcohol and its derivatives,

constitute the true elements of organic nature, while the simplest constituents, such as C, H, O, and N, only appear when the organic substance is destroyed." Moreover, in 1838, Liebig gave three characteristics for determining a compound radical, using cyanogen as a text. "We term cyanogen a radical, because (1) it is the unchanging constituent of a series of compounds; (2) because it is capable of replacement on these by simple substances and (3) because, in those where it is combined with one element, this latter can be exchanged for its equivalent of another element." This Radical Theory did much good by inducing chemists to examine the true constitution of organic compounds through inorganic knowledge.

It had been noticed by this time that when certain compounds were acted upon by Cl as much H was separated as was equivalent to the entering Cl. The attention of Dumas was called to this, while he was trying to discover the cause of the hydrochloric acid fumes coming from the wax candles of the Tuilleries. His work upon the production of chloral from alcohol also bore upon this question. But his crowning achievement was the discovery of trichloroacetic acid- an acid in which chlorine had replaced, ordinary acetic acid, without altering its chief characteristics as a monobasic acid. The facts of substitution, the exchange of electro-negative chlorine for electro positive hydrogen, without essentially changing the nature of the compound, overthrew the electro chemical dualistic theory of Berzelius. Berzelius himself did as much as any one man to weaken his position. He abandoned the search for truth to spin wild hypotheses in explanation of these newly discovered substances.

In 1834, Dumas published the following empirical rules of Sub-

stitution.

1. "When a compound containing hydrogen is exposed to the dehydrogenising action of chlorine, bromine, etc. for each atom of hydrogen that it loses.
2. "If the compound contains water it loses the hydrogen of this without replacement." Laurent declared that these rules were not true in all cases. Moreover it was Laurent who said that chlorine performed the same work in the compound as the hydrogen it replaced. Dumas vigorously opposed these views until his own discovery of trichloroacetic acid forced him to accept them, and to subscribe to Laurent's Nucleus Theory.

This Nucleus Theory, however, was never very popular. All organic compounds were supposed to either "original nuclei," made from the first by the substitution of hydrogen for other elements, or by the taking up of additional atoms. This theory did away with the old idea that radicals were unalterable.

The Older Type Theory of Dumas arose from the facts of substitution. After the discovery of trichloroacetic acid in 1840, Dumas announced that when a halid replaces hydrogen, atom for atom, in an organic compound, the new substance, and the older hydrogenated one belong to the same type. They belong to the same chemical type when the fundamental properties are preserved after the composition has been changed. They belong to the same mechanical type when the fundamental properties are modified although the number of atoms remains unchanged. This idea of mechanical types was adopted by Dumas from the views of Regnault.

From the way in which Dumas viewed chemical combinations grew the idea of unitarism, as opposed to the dualism which he had over-

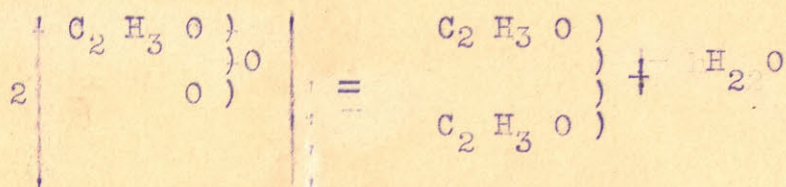
thrown. Dumas conceived a compound to form a whole, any constituent atom of which could be replaced, and yet leave the compound intact.

In this early form, the type theory was incapable of generalization. It admitted as many types as there were primitive combinations, and established no connection between them. The work of the followers of Dumas was "to refer all organic and inorganic compounds to a small number of types, chosen so as to represent different forms of combination."

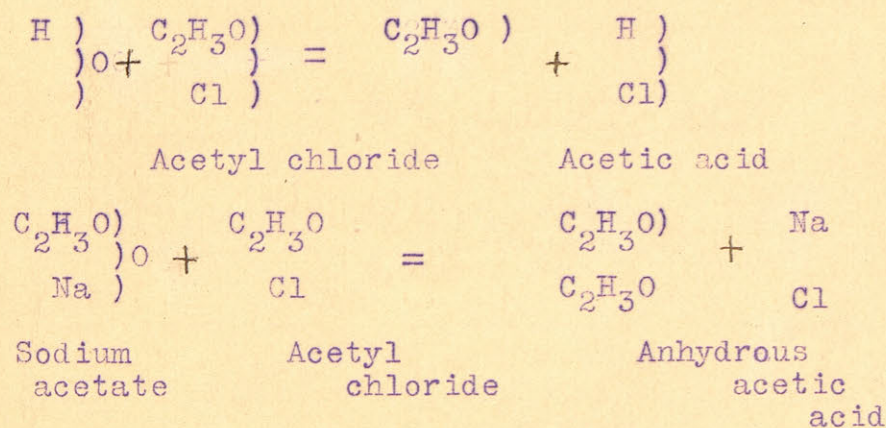
Laurent first established the water type, comparing certain oxides of water. "Hydrate of potassa" or potassium hydroxide was to him, water in which one atom of hydrogen had been replaced by one atom of potassium. Anhydrous oxides, such as Ag_2O , are water in which two atoms of silver are substituted for the two atoms of hydrogen. This began the later development of types. Dr. Williamson satisfactorily proved that if the molecule of alcohol contains one ethyl group, (C_2H_5) that of ether contains two; and he compared both compounds not only with water but also with the hydrates and oxides of inorganic chemistry. Acids, salts, and compound ethers were looked upon as combinations of the same order, and referred to the water type. Thus:--

Type	Acids	Salts	Compound Ethers
H) O) H)	NO_2) O) H)	NO_2) O) K)	NO) O) C_2H_5)
Nitric	Nitric	Potassium nitrate	Ethyl nitrate
	$\text{C}_2\text{H}_5\text{O}$) H) O	$\text{C}_2\text{H}_5\text{O}$) Na) O	$\text{C}_2\text{H}_5\text{O}$) O) C_2H_5)
	Acetic	Acetate of Soda	Ethyl acetate

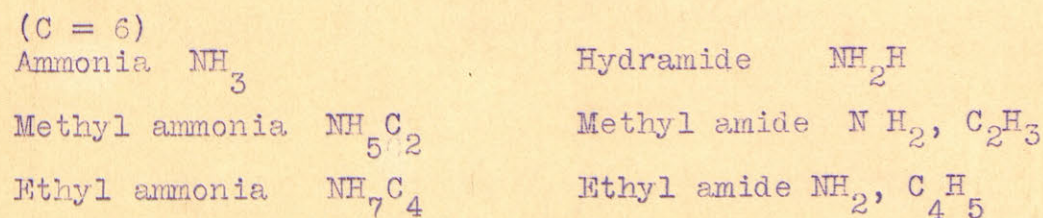
Gerhardt's discovery of anhydrous acetic acid also confirmed the idea of a water type:



While the following reactions of acetyl chloride proved that the hydrogen of water can be replaced by an organic radical:

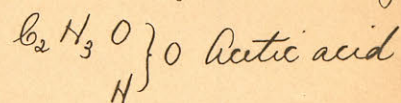
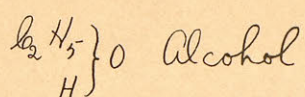


The ammoniacal type was established by Wurtz's discovery of the compound ammonias in 1849. Wurtz says: "I remarked that these bodies may be looked upon as simple ethers in which the equivalent of amidogen, or as ammonias in which an equivalent of hydrogen is replaced by methylum C_2H_3 , or by ethylium C_4H_5 . I expressed the relations existing between these bodies and ammonia by the following formulae:-

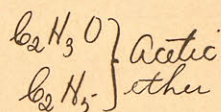
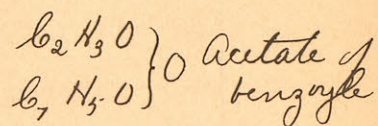
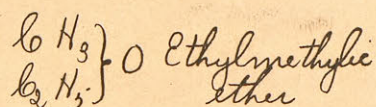
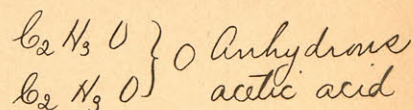
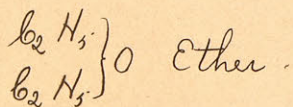


Besides the idea of regarding ammonia as the combination of the

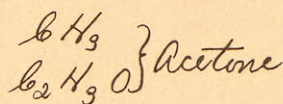
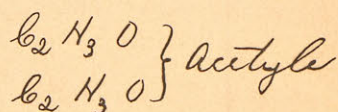
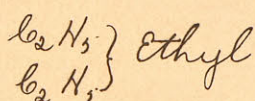
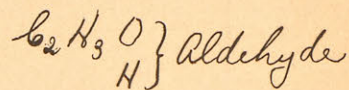
Left, or positive extremity Intermediate terms Right, or negative extremity



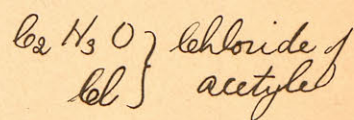
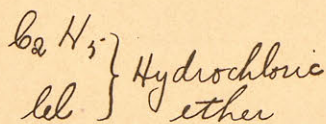
Water
Type $\left. \begin{array}{c} H \\ H \end{array} \right\} O$



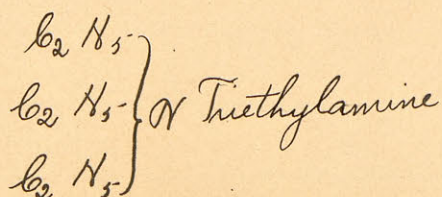
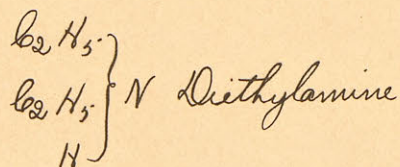
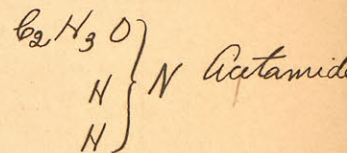
Hydrogen
Type $\left. \begin{array}{c} H \\ H \end{array} \right\}$



Hydrochloric
acid
Type $\left. \begin{array}{c} H \\ Cl \end{array} \right\}$



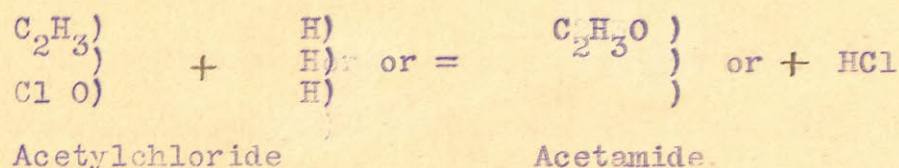
Ammonia
Type $\left. \begin{array}{c} H \\ H \\ H \end{array} \right\} N$



ammoniacal compounds was introduced of itself by a comparison of their properties. Whatever it might be, the ammoniacal type was established."

Gerhardt added two more types. Under the hydrogen type he placed organic radicals, aldehydes, and acetones. Under the hydrochloric acid type, which is itself a division of the hydrogen type, he united the organic and inorganic halides. Moreover he systematized all four types. The following table is one of Gerhardt's.

Gerhardt said that all types were types of double decomposition; that when molecules conflict together, an exchange always takes place between the atoms. Gerhardt was led by reactions such as the following,



To classify the amides under the ammonia type. The amides differed from the "alkaloids" (or amido- compounds) by the oxygenated nature of the radical.

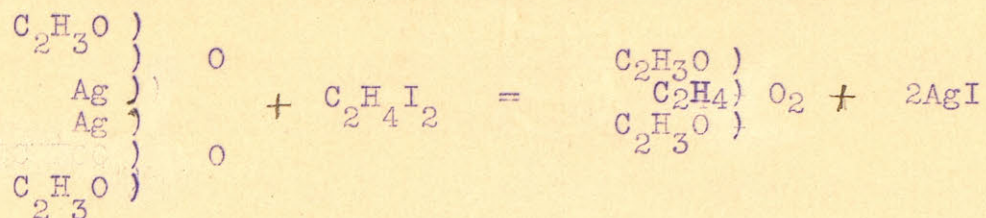
The properties of compound bodies are a function of the nature of the constituent atoms as well as of the grouping. Gerhardt arranged his table on the view that, starting from the neutral substance, water, either acids or bases could be formed, as the hydrogen was replaced by varying substances.

Dr. Williamson proposed his "condensed type" to explain polybasic acids. Thus sulphuric acid, H_2SO_4 , which could not be referred to one molecule of water could be disposed of comfortably by this means--



The bibasic radical sulphuryle (SO_2) replaces the hydrogen of two molecules of water, binding the remainder closely together. So also Wurtz showed that "two molecules of acetate of silver are bound together by the diatomic radical ethylene when iodide of ethylene

reacts on acetate of silver."



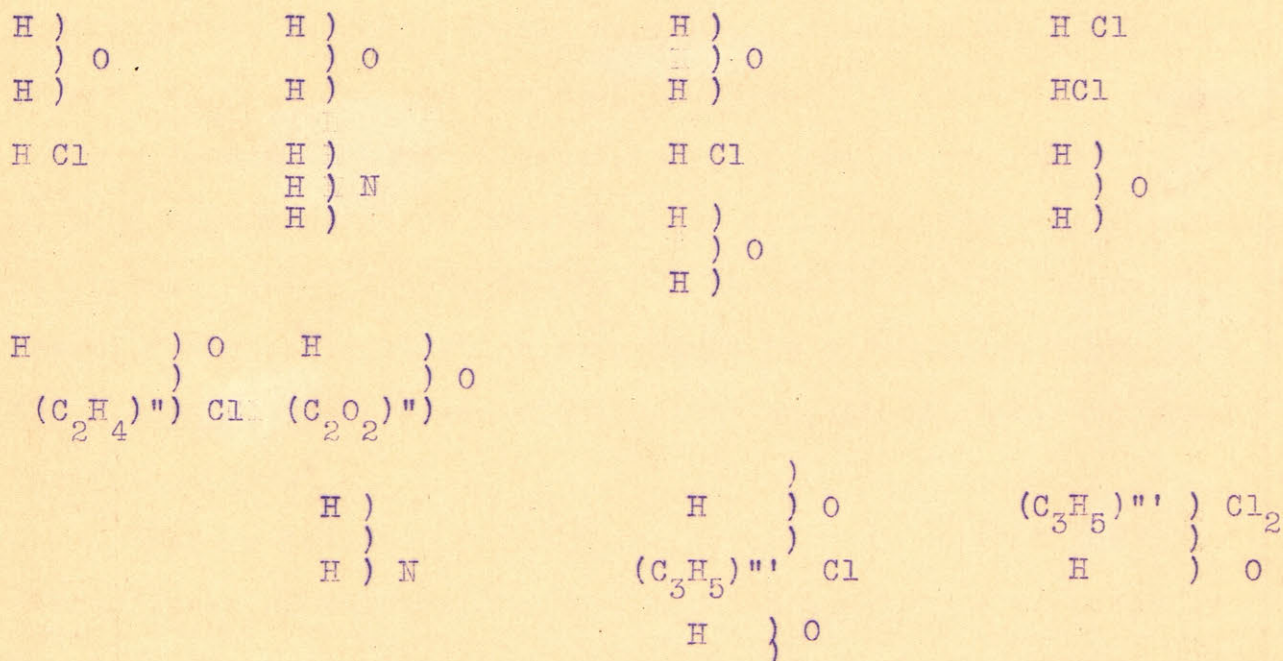
Thus Dr. Williamson and Gerhardt had referred the polybasic acids, Dr. Odling the polyacid bases, and Wurtz the poly atomic alcohol, to the doubly or trebly condensed water type. In 1858, Canizzaro, an Italian first considered certain metals as diatomic, and so connected various inorganic hydrated bases with organic alcohols.

Type	Hydrated Inorganic Bases	Alcohols	Inorganic Acids	Organic Acids
$\begin{array}{c} \text{H}_2 \\ \text{H}_2 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_2$	$\begin{array}{c} \text{Ca}'' \\ \text{H}_2 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_2$	$\begin{array}{c} (\text{C}_2\text{H}_4)'' \\ \text{H}_2 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_2$	$\begin{array}{c} (\text{CO})'' \\ \text{H}_2 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_2$	$\begin{array}{c} (\text{C}_2\text{H}_2\text{O})'' \\ \text{H}_2 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_2$
	$\begin{array}{c} \text{Ba}'' \\ \text{H}_2 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_2$	$\begin{array}{c} (\text{C}_3\text{H}_6)'' \\ \text{H}_2 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_2$	$\begin{array}{c} (\text{SO})'' \\ \text{H}_2 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_2$	$\begin{array}{c} \text{C}_2\text{O}_2 \\ \text{H}_2 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_2$
	$\begin{array}{c} \text{Cu}'' \\ \text{H}_2 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_2$	$\begin{array}{c} (\text{C}_5\text{H}_{10})'' \\ \text{H}_2 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_2$	$\begin{array}{c} \text{P}''' \\ \text{H}_3 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_3$	$\begin{array}{c} \text{C}_2\text{H}_4\text{O} \\ \text{H}_2 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_2$
$\begin{array}{c} \text{H}_3 \\ \text{H}_3 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_3$	$\begin{array}{c} \text{Sb}''' \\ \text{H}_3 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_3$	$\begin{array}{c} (\text{C}_3\text{H}_5)''' \\ \text{H}_3 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_3$	$\begin{array}{c} (\text{PO})''' \\ \text{H}_3 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_3$	$\begin{array}{c} (\text{C}_3\text{H}_3\text{O}) \\ \text{N}_3 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_3$
	$\begin{array}{c} \text{Bi}''' \\ \text{H}_3 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_3$	$\begin{array}{c} (\text{C}_5\text{H}_9)''' \\ \text{H}_3 \end{array} \left. \begin{array}{c}) \\) \end{array} \right\} \text{O}_3$		

A polyatomic radical moreover can unite several molecules of hydrogen or ammonia, and thus the idea of compound types can be widely extended.

The general principle is, that several molecules are united into a more complex one, because, in each of them, an atom is replaced by a single element or indivisible group.

Dr. Odling of Oxford elaborated Mixed Types, those wherein a polyatomic radical or an element connects several molecules of different natures. The following formulae illustrate this idea:



This Type Theory and the notation implied in it, were helpful in classifying and explaining various facts. But questioning soon arose as to whether it was more than a means of convenient tabulation, whether or not it was subordinated to some general principle which explained its existence. Kolbe, especially, attached it as arbitrary and unscientific. "How can we admit," he said, "that nature could so restrict herself as to form all organic and inorganic combinations in the mould of four substances chosen at hazard-- hydrogen, hydrochloric acid, water, and ammonia -- and to produce nothing but variations on these four themes? Further, what natural connection is

there between the majority of organic compounds, and H_2O , hydrogen, or hydrochloric acid?"

Replying to these objections, Wurtz says: "The types are not chosen at hazard, but represent three forms of combination, between which the theory can form a connection. We may in a manner reduce these types to one, and refer them to hydrogen more or less condensed. Thus water is hydrogen doubly condensed, in which one diatomic atom of oxygen has replaced two atoms of hydrogen. A water type exists because there exists a diatomic element, oxygen; and we are justified in admitting an ammonia type because there exists a triatomic element, nitrogen.----- The types are not chosen at hazard, since they represent forms of combination determined by a fundamental property of the elements; their power of substitution, their combining power, their atomicity."

Before going on to note the development of this theory of atomicity or of valency, we must mention a new type proposed by Kekule, almost simultaneously with the development of mixed and condensed types. Apropos same investigations upon fulminate of mercury Kekule said that the methyl compounds and their derivatives might be referred to the type of marsh gas, to which he gave the formula C_2H_4 ($H = 1$, $C = 6$, $O = 8$). To illustrate this idea the following formulae may be given:

C_2H_4	C_2H_3Cl	C_2HCl_3	$C_2H_3C N$	$C_2Cl_3NO_4$
Methyl hydride	Nethyl chloride	Chloroform	Aceto-vitril	Chloro- picrin

In 1858, Kekule published a paper "On the Constitution and Metamorphoses of Chemical Compounds and on the Chemical Nature of

of methyl and carbonyl, and so on. These results and those obtained by Frankland were of such great importance as to be almost indispensable for the development of the type theory into the structural theory. The chief merit for having determined that the peculiarities of the various types rested upon the different saturation capacities of the elements contained in them, belongs to Frankland.

It was from his work on the organometals that Frankland deduced the kernel of the theory of valence proper. Before his time Bunsen had done his work on the cacodyl compounds, and Kolbe had designated cacodyl as arsene dimethyl. Relying upon these researches and upon his own work on the stannosethyl compounds, Frankland first destroyed the theory of copulae, by showing that the power of metals to combine with oxygen is altered by copulation with radicals. According to his views, the so-called copulated compounds are derivatives of inorganic bodies in which oxygen is replaced by its equivalent of hydrocarbon radicals. Thus, stannos-ethyl oxide is SnO_2 in which one equivalent of oxygen is replaced by ethyl. He then proceeded to extend this conception to other compounds, and so harmonized the laws shown in the composition of organic and inorganic substances with the fundamental properties of the elements which these contain.

"It is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that no matter what the combining power of the attracting element, if I maybe allowed the term, is always satisfied by the same number of these atoms."

This doctrine of atomicity, or as we now say, of valency, was implied in the facts leading to the laws of combining volumes and of multiple proportions, but Frankland was the first to see the meaning

Carbon," which applied to carbon the principles already applied to nitrogen and its chemical analogues. He said that carbon was tetratomic. "If we look at the simplest compounds of this element, CH_4 , CH_4Cl , CCl_4 , CHCl_3 , COCl_2 , CO_2 , CS_2 and CHN , we are struck by the fact that the quantity of carbon which is considered by chemists as the smallest unit capable of existence - - the atom - - always binds four atoms of a monatomic or two of a diatomic element, so that the sum of the chemical units of the elements combined with one atom of carbon is always equal to four. We are thus led to the opinion that carbon is tetratomic." In making these statements, Kekule was merely following the line of reasoning by which Frankland had already deduced the trivalence and penta valence of nitrogen, phosphorus, arsenic, and antimony; and by which both Kolbe and Franklin had already recognised the tetravalence of carbon.

We have already mentioned Kolbe's opposition to the type theory. Yet it has been frequently asserted that he was influenced by Gerhardt's type doctrine, and that his derivation of organic compounds from carbonic acid, carbonic oxide, sulphuric acid, sulphurous acid etc. coincided with that from the three types, hydrogen, water, and ammonia. It is true that Kolbe connected organic with inorganic compounds, but his types, as opposed to the formal ones of the typists were real. He tried to prepare organic substances artificially from simple inorganic substances, with a view to gaining an insight into their chemical structure. While, in the type theory, radicals were looked upon as residues whose nature could be no further investigated. Kolbe tried to break up radicals into their immediate constituents. Thus he showed cacodyl to be arsene dimethyl, acetyl to be a compound

of facts well known to all chemists, and to express this idea in a definite form. Kekule and others have developed this theory, but credit should be given to Frankland as its originator.