PRIMARY DOCUMENTS
"ON THE DIFFERENT EXPLANATIONS OF CERTAIN CASES OF ISOMERISM"

Mr. A. Boutlerow
"Sur les explications différents de quelques cas d'isomerie,"
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Translated by David E. Lewis

Research in modern times has enriched the science by the discovery of some very instructive cases of isomerism, and shortly afterwards different attempts at a theoretical explanation of these facts appeared. The authors of some of these explanations, especially Messrs. Kolbe and Kekulé, appear, at first glance, to have chosen dissimilar starting points and have arrived at different conclusions. The explanations given by one, as by the other of these writers, merely consist of the difference in what one calls the chemical constitution of bodies. Although it is generally thought that the ideas of Mr. Kolbe and those of Mr. Kekulé on chemical constitution have no resemblance to each other, I believe that I can prove that their theoretical views are based on the same, or nearly the same fundamental principles, and that the difference in their conclusions is explained by the fact that these principles are not always applied in a manner that is sufficiently general and sufficiently rigorous. Now that we are beginning to move on from the school of Gerhardt, it is not difficult to note that the ideas formerly expressed by French chemists, and those of their opponents, were not always very far from each other. Sometimes, the difference lay in the form, rather than in the substance of these ideas.

Thus, on the basis of some theoretical views of Mr. Frankland, Mr. Kolbe is seen to express his thoughts on the saturation capacity of the elements (1) and at almost the same time, to pronounce himself vigorously opposed to the mechanical types of Mr. Dumas. Now, however, it is clear that these types only represent one way to express the saturation capacity of the elements, and that the new theoretical ideas of Mr. Kolbe, designed to explain the natural relationships between organic substances and mineral compounds, are themselves founded on the same principle—that of valence. By reading the classical treatise of Gerhardt and the treatise of Mr. Kolbe, one can well see that the two chemists attach a different significance to the word *constitution*, and that, at the same time, Gerhardt himself is almost forced to speculate on the chemical *constitution*, if one acknowledges this word in the sense that Mr. Kolbe gives to it. For Gerhardt, the molecular constitution is *the actual arrangement of the atoms* (2), and it is in the same sense that this term is accepted by Mr. Kekulé (3), while Mr. Kolbe speaks only of *points of attack* (Angriffs-Puncte) *of affinity*, and does not even believe that one day one might be able to judge the relative positions of the atoms in space (4). [The italics in this paragraph, and elsewhere in the translation, are in the original, unless otherwise noted. —DEL] At the same time, Gerhardt, seeking to interpret the action of chlorine on ethylene as a double decomposition *without the hydrogen chloride formed being released* (5), apparently acknowledges the possibility of judging the pre-existence of a fully-formed substance (hydrogen chloride) in the composition of the other, more complex, compound. The ideas of Mr. Kekulé on the possibility of determining the rational constitution of substances appear to be to be even

less removed from those of Mr. Kolbe, but the assertion of Mr. Kekulé that type formulas are only transformation formulas for substances (Umsetzungs-Formeln) (6) is likely, I believe, to throw this question into a certain obscurity. It is true that these formulas do not describe the constitution, if you wish to understand by this word the position of the atoms in space; but, at the same time, it is clear that Mr. Kekulé's formulas are intended, most often, to describe the chemical relationship of the elementary atoms that enter into the composition of the molecule (the points of attack of affinity, the constitution in the meaning given to this word by Mr. Kolbe). On the other hand, if one recalls the sense that Mr. Kolbe attaches to the word constitution, one cannot, for example, see in his hypothesis related to acetic compounds a way to describe the chemical bond that exists, 1) between the two carbon atoms, 2) between one of these atoms and an atom of oxygen, and 3) between the other carbon atom and three atoms of hydrogen. At the same time, it is evident that Mr. Kekulé, while speaking, for example, of the two molecules of water joined by the radical $\overline{SO}^2$ in a molecule of hydrated sulfuric acid, considers the two HΘ residues as the points of attack for the affinity of the sulfuryl radical. Further on, Mr. Kekulé explains himself on the same subject in a much clearer manner (7): *"These atoms," he says, "are linked to carbon in an indirect manner, through oxygen or nitrogen," or, "by the type of hydrogen, that is to say, one that is backed (anliegend) (8) by an atom of oxygen and not united with carbon except by means of this last atom."*
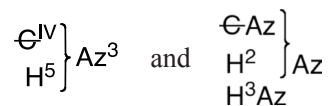
Messrs. Kolbe and Kekulé both want to determine the manner in which the elementary atoms are chemically linked to each other in a compound molecule. Mr. Kolbe designates this manner by the word *constitution*; for myself, I prefer the name *chemical structure*, a term to which no different meanings have yet been attached, and which, for that reason, is less likely to give rise to misunderstandings (9). I do not believe that it may be impossible, as Mr. Kekulé thinks (10), to specify on a map the position of the atoms in space: it is clear that mathematical formulas may well do it, and it is to be hoped that the laws that govern the formation of chemical molecules will one day find their expression with mathematics. I do not believe, either, with Mr. Kolbe, that once the existence of atoms is recognized, we would never get to determine their positions in space. I think it is useful for the moment to leave aside the atomic hypothesis that, although probable, is not yet necessary for our purely chemical considerations.

Whatever may be, it is clear that the theoretical considerations of Mr. Kekulé, as well as those of Mr. Kolbe, are based on the same principle, that of chemical structure. Since the important role of valence was recognized, this principle serves as the starting point for almost all theoretical views. It is found in the considerations of Mr. Wurtz on isomerization in hydrocarbons, in the radicals typical of Mr. Heintz and in the formulas of Mr. Wislicenus. It is two years since I tried to draw the attention of chemists to the necessity of substituting this principle for older theoretical ideas (see memoires on chemical structure, and on the affinities of polyvalent atoms, etc.). A sufficiently broad application of this principle, with all its consequences, will, I believe, be capable of settling all the disagreements that currently separate chemist theoreticians, while an application of the same principle with only little rigor will only serve to create new difficulties. That's how the difference in the formulas used by Messrs. Kolbe and Kekulé prevents their agreement, while, in going further, seeking the true meaning of these formulas, going back to the principle on which they are based, one recognizes that the difference is more apparent than real. One also sees that the rigorous application of the fundamental principle must lead to specific changes to erase the differences between the two chemists. After having accepted the principle of the chemical structure, one cannot say, as does Mr. Kekulé, that a substance can have several rational formulas, and one no longer has the need of types, which add nothing to the understanding of the formulas.

The facts lead to the admission that atoms act with a limited quantity of chemical combining power, and that each one of two atoms chemically linked one to the other uses, for this bond, at least one unit of its force. Thus, one unit of chemical combining power cannot act at the same time on two different atoms, and consequently it is clear that one formula describing the manner in which all the atoms of a molecule are chemically joined together must remain invariable, until it was acknowledged that the chemical bond of atoms is not what it describes. In every case, for one substance there is one and only one possible, truly rational formula. It is true that such a formula may have different forms; it could also be more or less complete as it describes the way in which all the atoms, or only some of them, are linked in the molecule, but it will always be the same formula, with more or less detail. Thus, one does not have the right to apply, at the same time, the two formulas

$$Az^2\left\{\begin{array}{l}C^{IV}\\H^2\end{array}\right. \quad \text{and} \quad Az\left\{\begin{array}{l}\overset{\prime}{C}Az\\H^2\end{array}\right.$$

to cyanamide, or the two formulas

$$\left.\begin{array}{l}C^{IV}\\H^5\end{array}\right\}Az^3 \quad \text{and} \quad \left.\begin{array}{l}CAz\\H^2\\H^3Az\end{array}\right\}Az$$
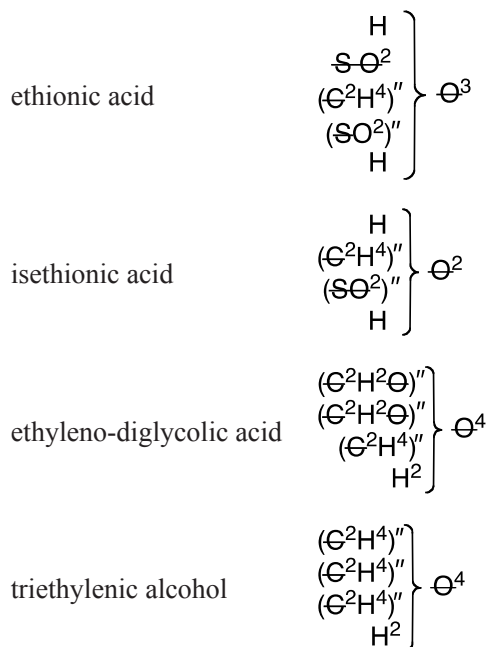
to guanidine (11). By following the principle that Mr. Kekulé himself accepts, we arrive at the conclusion that the first of these formulas does not have a well-defined meaning; it can be viewed as identical to the second formula, or it represents cyanamide as a combination of two divalent groups with the carbon atom, C, that is to say, as $C^{IV}2(\overset{\prime\prime\prime}{Az}H)''$; while the second formula positively expresses the idea that the substance in question contains an atom of cyanogen united with a monovalent residue of ammonia

$$\left.\begin{array}{l}(C^{IV}Az)'\\H^2Az\end{array}\right\}$$
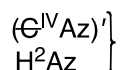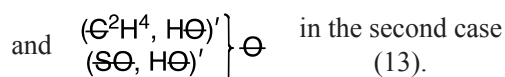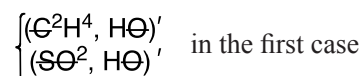
However, it is not immaterial whether one considers one atom of nitrogen joined to carbon by means of 3 units, and the other by only one unit of chemical combining power, or whether one thinks of each of the two nitrogen atoms joined to the carbon by two units of this force. From the first formula of guanidine, this base is formed by the union of C with $(AzH)''$ and $2(AzH^2)'$; from the second, it is the combination of C with Az''' and AzH^2 and with AzH^3, which is not at all the same thing. At the same time, the last formula of guanidine does not satisfy the demands of the principle of valence; the affinity of the carbon atom being saturated by Az''' and $(AzH^2)'$, this atom can no longer bind to ammonia. To represent the nitrogen of ammonia as acting, in this case, with all five units of its force, would be to allow the joining of the nitrogen atoms to each other. Among the formulas given by Mr. Kekulé, there are again, some that likewise contradict the principle of valence. The formula that he gives for acetal, for example, represents this substance (12) as resulting from the union of C^2H^4O with two atoms of ethyl joined by O, that is to say, as a combination of two saturated molecules. From the formation of acetal, it appears much more likely that it is analogous to the diethyline of glycol [ethylene glycol diethyl ether —DEL], and that the difference between these two substances resides only in the difference between ethylene and ethylidene. The two substances would therefore be combinations of a divalent radical, C^2H^4, with two

monovalent groups, $2(C^2H^5,O'')'$. Other formulas by Mr. Kekulé do not clarify the question of the manner in which the oxygen placed after the parenthesis serves to hold the different constituent parts in the molecule. These are the formulas of

ethionic acid $\quad\left.\begin{array}{c}H\\SO^2\\(C^2H^4)''\\(SO^2)''\\H\end{array}\right\}O^3$

isethionic acid $\quad\left.\begin{array}{c}H\\(C^2H^4)''\\(SO^2)''\\H\end{array}\right\}O^2$

ethyleno-diglycolic acid $\quad\left.\begin{array}{c}(C^2H^2O)''\\(C^2H^2O)''\\(C^2H^4)''\\H^2\end{array}\right\}O^4$

triethylenic alcohol $\quad\left.\begin{array}{c}(C^2H^4)''\\(C^2H^4)''\\(C^2H^4)''\\H^2\end{array}\right\}O^4$

It appears possible to me to suppose that isethionic acid contains either the sulfuric acid radical, $(SO^2)''$, or that of sulfurous acid, $(SO)''$, as Mr. Carius thinks.

The formula showing the structure of this acid would be:

$$\left[\begin{array}{l}(C^2H^4, HO)'\\(SO^2, HO)'\end{array}\right. \quad \text{in the first case}$$

$$\text{and} \quad \left.\begin{array}{l}(C^2H^4, HO)'\\(SO, HO)'\end{array}\right\}O \quad \begin{array}{l}\text{in the second case}\\(13).\end{array}$$

According to the first formula, the sulfur is directly linked to carbon, and according to the second, it is indirect, by means of the oxygen. In both these assumptions, one of the two residues, being joined to the hydrocarbon radical, must have the character of an alcohol; the other, linked to an oxygenated radical, must possess acidic properties, that is to say, those that characterize the same residue in acids. Based on the first assumption, which appears to be the more probable, isethionic acid would be closer to glycolic and lactic acids and their homologues. The difference between sulfurous and sulfuric acids would be due, based on the quantity of the chemical

combining power with which the sulfur acts. This element appears as tetravalent (S^{IV}) in the first, and as hexavalent (S^{VI}) in the second of these acids. The existence of the anhydrides SO^2 and SO^3 gives a certain degree of probability to the latter assumption.

Since the development of the ideas of valence, the meaning of Gerhardt's types has become obvious. It has been recognized that the service rendered to science by these types lies in the simple and clear way that they describe the degree of molecular complexity produced by atoms of different valence. It was also recognized early on that the four primitive types are no longer sufficient to show all the complexity due to pentavalent nitrogen and its analogues. In cases where the complexity depends on the polyvalency of carbon, an element that does not appear in the make-up of types, it was necessary to double or triple the Gerhardt types. Finally, in cases where three, four, or several polyvalent elements at a time are the reason for the binding of atoms in a molecule, the introduction of compound types was attempted. This, due as much to habit as to a real need, has not been able to clarify anything. The original simplicity of type formulas is no longer found in the compound types, and that is all the more so as, the complexities of the molecules produced by the influence of several polyvalent elements at a time being almost uncountable, it has become necessary to create a huge number of compound types. At the same time, these types no longer offer those advantages that made Gerhardt's types so useful to science. Considered by themselves, compound types do not describe the complications that are characteristic of their derivatives. Thus, the type (14)
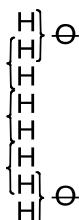

explains nothing by itself. It only has a meaning through the formulas of its derivatives, succinic acid and its homologues. As a molecule, this type is impossible: it does not satisfy the principle of valence. Compared to the formula of succinic acid, it only serves to point out the valence of the substituent residues, which can be done in an equally understandable and much more simple way by the accents (′) placed above or alongside formulas, and which are already in general use. Finally, the type formula given for succinic acid by Mr. Kekulé would make one believe that the HѲ residues are joined to this

substance at the hydrocarbon group, while according to the theoretical ideas expressed by Mr. Kekulé himself, these residues are certainly combined with the carbonyl group, CѲ, and the two monovalent groups
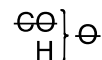
thus formed are linked to the divalent radical C^2H^4. This perspective, completely conforming to the views of Mr. Kekulé, can be expressed much more simply by a shorter formula, and without the need to derive any type; for example:
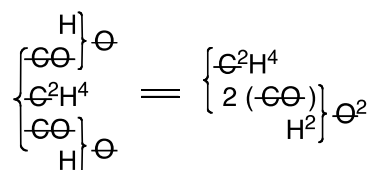

In similar fashion, all other types are henceforth useless; the valences of atoms and residues, molecular complexities, and the analogues of substances can be designated without the use of types, which are only capable of describing that valence, those complexities, and those analogies.

Mr. Kolbe, like Mr. Kekulé and most other chemists, acknowledges that the elements are endowed with a limited quantity of chemical combining power, and that on the amount of valence of the elements depends the valence of compound residues. Thus, he views the "carbonyle" carbon, $C = C^2$, as the only cause of the trivalency of formyl C^2H, in which the fourth affinity of carbon is saturated by the atom of hydrogen (15). [This is not equivalent to a modern carbonyl carbon, >C=O, but, rather, to a modern methylene carbon, >C=. The author uses the same term with both meanings, so careful attention to context is required. —DEL.] These considerations of Kolbe, quite consistent with the prevalent theoretical views, necessarily imply the existence of saturated molecules, and lead to the examination of the manner in which the elementary atoms are linked in the molecule formed (chemical structure). These views are not modified one bit if one writes C^2 in place of C, and if one speaks of the carbonyl instead of an atom of carbon.

For Mr. Kolbe, as for everyone else, it is a fact that the minimum amount of carbon entering into chemical combinations is equal to 12, and that this minimum quantity is, furthermore, tetravalent. Like everyone else, he cannot yet explain why this quantity of carbon is neither less than 12, nor possesses another valence. But, by rigorously applying the principle that he acknowledges,

Mr. Kolbe must necessarily admit that when the chemical combining power of an atom or group is saturated, that atom or group becomes, as a result, incapable of chemical bonding. He must also admit that: the unit of chemical combining power residing in the methyl group belongs to the carbon atom; that trimethylamine contains three methyl radicals, because the nitrogen acts with three of its units of force; that, as a consequence, the nitrogen in this base is attached directly to the carbon, while the hydrogen, combined with the atoms of carbon, is only retained in the molecule by means of the latter element, and is in no way directly bonded to the nitrogen.

When considering ethylene, with Mr. Kolbe, as

$$\left.\begin{array}{c} C^2H^3 \\ H \end{array}\right\} C^2 \;=\; \left[\begin{array}{c} \text{---CH}^3 \\ \text{---CH} \end{array}\right.$$
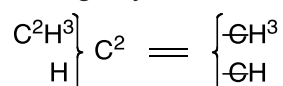
one evidently describes by this formula that the two carbon atoms are combined with each other by two units of affinity, that one atom of carbon is united to three, and the other to one atom of hydrogen, and that, as a consequence, the free affinities possessed by ethylene belong to one of the two carbon atoms encompassed by the molecule of ethylene.

We can ignore the question of the greater or lesser probability of this view. Still, however that may be, this is how one must interpret the formulas of Mr. Kolbe, if one wants to rigorously apply the fundamental principle acknowledged by him, and identical, as we have seen, to that which serves as the point of departure to the theoretical considerations of Mr. Kekulé and several other chemists.

Eventually it becomes necessary to examine not only the way in which the radicals, but also that in which the elementary atoms are combined into a compound molecule. At the same time, it must be allowed that each atom entering into the composition of the molecule is held there by the chemical combining power belonging to it and to another elementary atom.

These are, I believe, the necessary consequences of the principle [of valence —DEL]. However, Mr. Kolbe does not venture that far; he stops at examining radicals and how they combine, without entering into the details of the chemical structure of the radicals themselves. At the same time, he appears to allow the possibility of the combination of two saturated molecules (16). Analogous considerations, little compatible with the fundamental principle acknowledged by Mr. Kolbe are, in my opinion, the main reason for the disagreement that his theoretical views inspire with other chemists at the present time.

Thus, the formula HO (= 9) for water and the atomic weight O = 8 that Mr. Kolbe continues to use remove all resemblance to the type formulas of Mr. Kekulé.

Mr. Kolbe appears to agree, now, that the vapor density of substances is one *criterion* for determining their molecular weights, and we know that among the thousands of molecules measured, there is not a single authentic example of a substance containing one equivalent of oxygen (O = 8). But even if we do not pay attention to this circumstance, already very important, the ideas that Mr. Kolbe expresses on the ratio between carbon and other polyvalent elements are sufficient, by themselves, to lead to the adoption of the double atom of oxygen, $O^2 = \Theta$, and the formula $H^2\Theta$ for water.

For simple ethers and the anhydrides of monobasic acids, this scholar uses the generally acknowledged double formulas. Why and how are monobasic radicals bound in the molecule of the substance if the oxygen atom is not O = 16? And then, how will be explain the union of water with formula HO with the organic groups in the acid hydrates, etc.? In the molecule of acetic acid, $HO,C^2H^3(C^2O^2)O$, the valence of the tetravalent carbon (carbonyl = C^2) is completely saturated by the monovalent group C^2H^3 and by the 3 atoms of oxygen; on the other hand, the water, HO, is also a saturated molecule. So what, then, is the reason for the binding together of these two groups that do not possess the actual force to accomplish chemical combination? Likewise, the group

$$C^2H^4\left[\begin{array}{c} C^2O^2 \\ C^2O^2 \end{array}\right]O^2$$
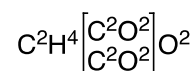
which Mr. Kolbe accepts in succinic acid combined with 2HO, being saturated, must be unfit to act chemically.

A large number of other formulas of this chemist give rise to similar observations. Is it not much more simple and more consistent to write $HO^2 = H\Theta$ instead of HO + O, and to consider this residue of a water molecule as monovalent and obeying the same principle with which Mr. Kolbe explains the trivalency of formyl C^2H, the monovalency of methyl, etc.? Is acknowledging the formula HO for water to deprive oneself, voluntarily, of the ability to trace the cause of the union of atoms in a group of complex compounds? I do not believe that using the old atom of oxygen and the formulas C^2O^2 and C^2O^4 for the oxide of carbon [carbon monoxide] and carbonic acid [carbon dioxide] are necessary to the views of Mr. Kolbe. It is true that many derivative organic substances cannot be obtained from these two compounds, as types, by way of substitution, but the theory loses nothing from that. Other types, like ΘH^4 or ΘCl^4 can render the same

service. For the theoretical views of Mr. Kolbe, like those of the majority of other chemists, it is essential that carbon be tetravalent, that it may also sometimes act with a part of its affinity, and that the atoms of this element have the capacity to bind to each other. The presence or absence of oxygen in compound types adds nothing to this perspective. In the formulas C^2O^2 and C^2O^4, the atoms of oxygen $O = 8$ are only representative of units of chemical combining power, and the symbols C'' and C^{IV} are then both types of the oxide of carbon and carbonic acid. One may hope, I think, that the molecular formula for water, $H^2\Theta = H^2O^2$ will soon be acknowledged by Mr. Kolbe, as he has already acknowledged the molecular formulas of ethers [esters —DEL] and anhydrides of the dibasic acids.

Now, if we introduce $H\Theta$ for $HO + O$ into the formulas of Mr. Kolbe, and if we compare them to the formulas of Mr. Kekulé, remembering that both are designed, in principle, to describe the chemical structure of bodies, one must admit that in the majority of cases, these formulas are identical.

	Formulas of Mr. Kekulé	Modified formulas of Mr. Kolbe
acetic acid	$\begin{matrix}\mathsf{CH}^3 \\ \mathsf{CO} \\ H\end{matrix}\bigg\}\Theta$	$=$ $\quad$ $\mathsf{CH}^3(\mathsf{CO})H\Theta$
		etc.
succinic acid	$\begin{matrix}\mathsf{CO} \\ \mathsf{CO} \\ H\end{matrix}\bigg\}\mathsf{C}^2H^4\Big\}\Theta$	$=$ $\quad$ $\mathsf{C}^2H^4\Big[\begin{matrix}\mathsf{CO}\\\mathsf{CO}\end{matrix}\Big]2H\Theta$
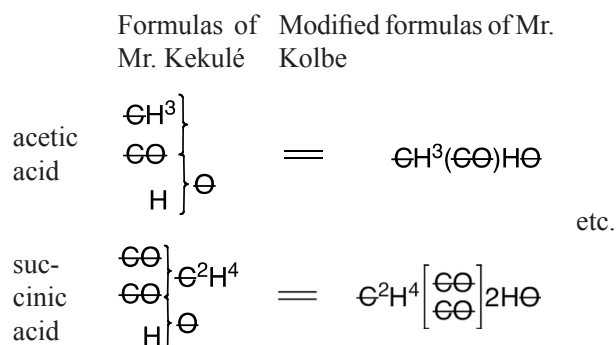
To make the meaning of these formulas yet more obvious, it would, perhaps, be useful to modify them a little by acknowledging that the parenthesis on the left indicates a bond between the carbon atoms, and writing

acetic acid $\left\{\begin{matrix}\mathsf{CH}^3\\\mathsf{CO}\\H\end{matrix}\right\}\Theta$ $\qquad$ succinic acid $\left\{\begin{matrix}\begin{matrix}H\\\mathsf{CO}\end{matrix}\Big\}\Theta\\\mathsf{C}^2H^4\\\begin{matrix}\mathsf{CO}\\H\end{matrix}\Big\}\Theta\end{matrix}\right.$
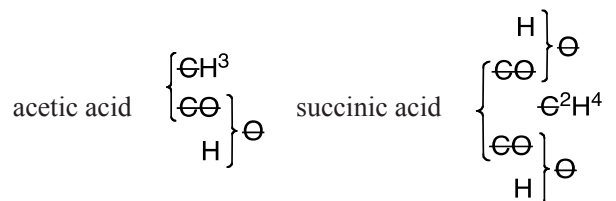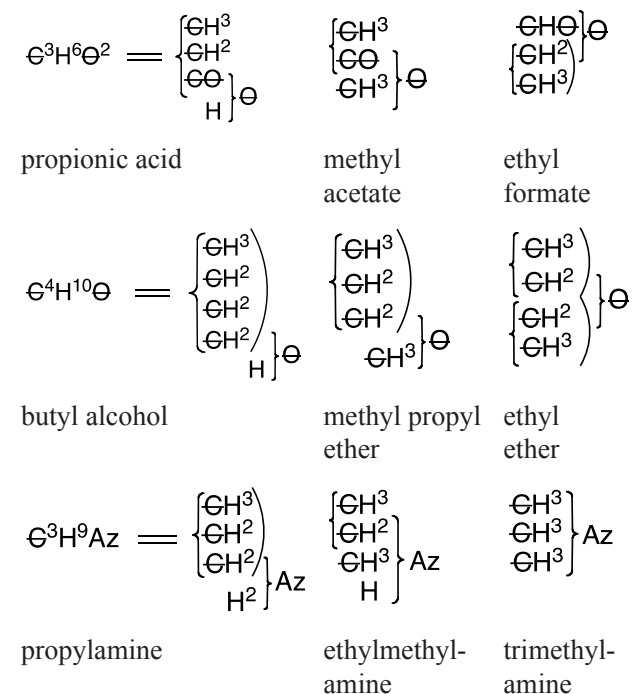
Finally, one must again note that the formulas of Mr. Kolbe often describe the details of the chemical structure better of molecules better than those of Mr. Kekulé. However, on breaking down these latter formulas, as Mr. Kekulé himself has done in certain cases, one generally arrives at *the same results*.

Passing onto the theoretical considerations by means of which Messrs. Kolbe and Kekulé seek to explain the isomerism of maleic and fumaric acids, etc., it will be noted first of all that the meaning of these views becomes especially clear when the principle of chemical structure, which serves as the starting point, is rigorously applied to the thoughts of these scholars as to their formulas.

To better understand the import of these thoughts, it is useful to realize the influence that the chemical structure of substances can generally exert on their isomerism.

The carbon atoms of an organic molecule are either joined directly through their affinity and a single polyvalent group that is bound further from other non-carbon atoms, or they form, by combining, several carbon-containing groups in which the carbon atoms, without being directly linked, are bound to the molecule through other polyvalent elements. In this way, we can produce a group of substances possessing the same molecular weight without being identical. This type of relationship between isomeric molecules is that which is ordinarily designated under the name of *metamerism*.

For example:

$\mathsf{C}^3H^6\Theta^2 = \left\{\begin{matrix}\mathsf{CH}^3\\\mathsf{CH}^2\\\mathsf{CO}\\H\end{matrix}\right\}\Theta \quad \left\{\begin{matrix}\mathsf{CH}^3\\\mathsf{CO}\\\mathsf{CH}^3\end{matrix}\right\}\Theta \quad \left.\begin{matrix}\mathsf{CHO}\\\mathsf{CH}^2\\\mathsf{CH}^3\end{matrix}\right\}\Theta$

propionic acid	methyl acetate	ethyl formate

$\mathsf{C}^4H^{10}\Theta = \left\{\begin{matrix}\mathsf{CH}^3\\\mathsf{CH}^2\\\mathsf{CH}^2\\\mathsf{CH}^2\\H\end{matrix}\right\}\Theta \quad \left\{\begin{matrix}\mathsf{CH}^3\\\mathsf{CH}^2\\\mathsf{CH}^2\\\mathsf{CH}^3\end{matrix}\right\}\Theta \quad \left.\begin{matrix}\mathsf{CH}^3\\\mathsf{CH}^2\\\mathsf{CH}^2\\\mathsf{CH}^3\end{matrix}\right\}\Theta$

butyl alcohol	methyl propyl ether	ethyl ether

$\mathsf{C}^3H^9Az = \left\{\begin{matrix}\mathsf{CH}^3\\\mathsf{CH}^2\\\mathsf{CH}^2\\H^2\end{matrix}\right\}Az \quad \left\{\begin{matrix}\mathsf{CH}^3\\\mathsf{CH}^2\\\mathsf{CH}^3\\H\end{matrix}\right\}Az \quad \left.\begin{matrix}\mathsf{CH}^3\\\mathsf{CH}^3\\\mathsf{CH}^3\end{matrix}\right\}Az$

propylamine	ethylmethyl-amine	trimethyl-amine

But there is also another kind of isomerism, to speak less broadly: all the carbon atoms in the two isomeric molecules are linked directly to each other in both cases.

Thus, two carbon atoms form the group $\begin{cases} C \\ C \end{cases}$ in glycol as well as in glycolamide; this group is bonded, in both substances, to $(AzH^2)'$, to $(HO)'$, to H^2, and to O, and yet these two substances are not identical.

This type of isomerism is explained by the mutual influence that atoms entering into the composition of a molecule exert on their reciprocal chemical character. Before specifying the details of this influence, it is essential to make an assumption, namely: each time that an atom acts with the same quantity of force in combining with other atoms, identical or not, it does not always act in the same way. This assumption does not, however, entirely abide by the facts: it is known that there are isomeric saturated hydrocarbons, C^nH^{2n+2}, and probably also isomers of methyl chloride, CH^3Cl. This has led me to acknowledge a difference in the units of force belonging to a carbon atom, that is to say, to acknowledge that two, or several atoms of carbon can combine with each other in different ways, and that a single atom of the same element can also combine in different ways with any other atom.

However, the influence of this difference is little known, and it appears probable that in every case it is less pronounced than the mutual influence of differing atoms entering into the composition of a molecule. The detailed study of the simplest organic compounds, those that contain only a single atom of carbon, promises to clarify the question of the differences in the units of chemical combining power belonging to that atom. However, until then it does not appear to be useful, in theoretical speculations, to take into consideration either this difference, or other, still problematic influences (the physical conditions under which the combination occurs, etc.). So, in choosing among the mutual chemical relationships of atoms where there is no doubt about the influence on their chemical character, and basing theoretical speculations only on these relationships, one can at least determine where the results of these speculations approach the truth, and what they still lack for that goal.

Having acknowledged the assumption mentioned above, we arrive at the following conclusions:
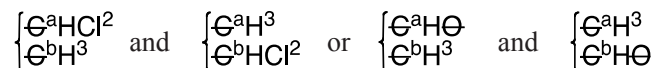
Two atoms of carbon or any element, each taken separately, must be identical; they must necessarily still remain identical while they are combined with each other or both with the same elementary atoms. Each time that these atoms combine with the same quantity of their chemical combining power, the same group is formed.

Thus, the groups

$$\begin{cases} C^{VI} \\ C \end{cases} \quad \begin{cases} C^{VIII} \\ C \\ C \end{cases} \quad \text{etc.}$$
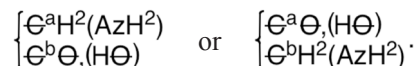
formed by the union of two or more carbon atoms must always have the same properties, and, as a consequence, the isomerism of two molecules formed by the union of such a group with other elements does not depend on the diversity of the groups formed by the carbon atoms. Two molecules having the same composition, and each containing, for example, the group $\begin{cases} C \\ C \end{cases}$ must remain identical if the role played by a carbon atom in the first case is filled by in the second by the other atom of this element. If we designate one of these carbon atoms by C^a and the other by C^b, and if these atoms are identical, then the two substances

$$\begin{cases} C^aHCl^2 \\ C^bH^3 \end{cases} \text{ and } \begin{cases} C^aH^3 \\ C^bHCl^2 \end{cases} \text{ or } \begin{cases} C^aHO \\ C^bH^3 \end{cases} \text{ and } \begin{cases} C^aH^3 \\ C^bHO \end{cases}$$

will also be identical. In the same way, it does not matter if glycine is

$$\begin{cases} C^aH^2(AzH^2) \\ C^bO,(HO) \end{cases} \quad \text{or} \quad \begin{cases} C^aO,(HO) \\ C^bH^2(AzH^2) \end{cases}.$$

In general, *two molecules having the same empirical composition must be identical and not isomers if the chemical relationship between each elementary atom and all the other constituent parts of the molecule is the same in both cases, and, at the same time, two or more atoms of carbon or any other element entering into the composition of a molecule cannot be distinguished from each other by differences in the chemical relationship between each of these atoms and the other constituent parts of the molecule.*

Two or more atoms of an element occurring in the composition of a molecule can and must be different from each other when the chemical relationship between each of them and the other constituent parts of the molecule is not the same. It does matter, for example, if the chemical structure of the substance CH^4Cl^2 is that described by the formula $\begin{cases} CHCl^2 \\ CH^3 \end{cases}$ or that described by the formula $\begin{cases} CH^2Cl \\ CH^2Cl \end{cases}$. In the first case, the chemical relationship is the same between each atom of the same element and all
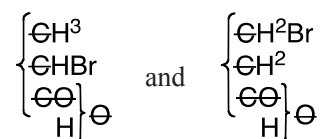
the other constituent parts; in the second case, it is the opposite. [It appears that Butlerov has reversed the two isomers here —DEL]

In glycine $\left\{\begin{array}{l} \text{CH}^2(\text{AzH}^2) \\ \text{CO,}(\text{HѲ}) \end{array}\right.$ and glycolamide $\left\{\begin{array}{l} \text{CO,AzH} \\ \text{CH}^2\text{HѲ} \end{array}\right.$, the chemical relationships of the constituent elementary atoms are no longer the same. The two atoms, identical in nature, on entering into the composition of the same molecule, take on a different chemical character when the influence exerted by each of them on the other constituent parts of the same molecule is different. The existence of this influence is a fact. It is easy to note that an element gives different relationships depending on the nature of the elements with which it is combined. Hydrogen atoms, for example, combined with carbon, behave with respect to other reagents in a manner other than those that are bound to oxygen, and this characteristic feature is conserved even within complex molecules. So it is that in alcohols, the hydrogen in the HѲ residue approximates the properties of the hydrogen of water, and the other hydrogen atoms, combined with carbon, generally give the same reactions as the hydrogen of hydrocarbons. Not only elementary atoms, but also compound groups influence the chemical character of atoms combined with them. The hydrogen of the residue HѲ, for example, while conserving the salient properties of hydrogen in water (oxidized hydrogen), behaves with reagents in different and characteristic ways depending on whether this residue is bound to a [modern—DEL] carbonyl carbon, in carboxylic acids, or a saturated alkyl carbon, in alcohols.
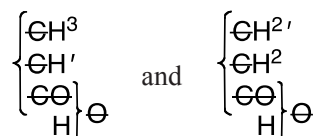
Thus, we see that the oxygen or hydrogen that is only bonded indirectly to the hydrogen of the HѲ residue, by means of carbon, nevertheless influences the character of the latter hydrogen. Based on such facts, we have the right to say, in general, as I have already noted in one of my previous papers, that elementary atoms in the interior of a molecule can exert a reciprocal influence on their chemical character without having to be directly linked. This explains the differences in the properties of glycine and glycolamide. In the first, the HѲ residue is combines with a carbonyl carbon as in an acid, and the AzH² residue is linked to a saturated alkyl carbon as in the amines. In the molecule of the second substance, the opposite takes place: the HѲ residue is bound to a hydrocarbon group, as in the alcohols, and the AzH² residue is combined with a carbonyl carbon as in the acid amides.

Of course, such facts naturally lead to the conclusion that the constituent atoms of a molecule can exert a reciprocal influence, though perhaps less pronounced,

when they are bonded in an even more indirect way. Thus, one will obtain, for example, two isomeric, non-identical substances from propionic acid by replacing one hydrogen of the saturated alkyl carbon combined with the group $\left.\begin{array}{l} \text{CO} \\ \text{H} \end{array}\right\}\text{Ѳ}$, by bromine, and then one hydrogen of the other saturated alkyl carbon:

$$\left\{\begin{array}{l} \text{CH}^3 \\ \text{CHBr} \\ \left.\begin{array}{l}\text{CO}\\ \text{H}\end{array}\right\}\text{Ѳ} \end{array}\right. \quad \text{and} \quad \left\{\begin{array}{l} \text{CH}^2\text{Br} \\ \text{CH}^2 \\ \left.\begin{array}{l}\text{CO}\\ \text{H}\end{array}\right\}\text{Ѳ} \end{array}\right. .$$
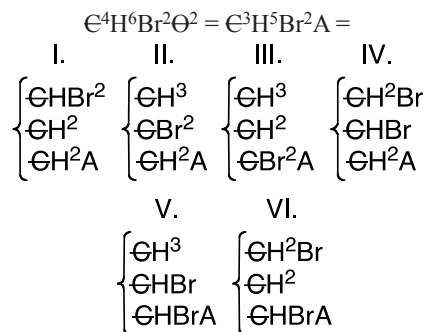
Speaking of the propionic acid residue $\text{Ꞓ}^3\text{H}^6\text{Ѳ}^2 - \text{H} = (\text{Ꞓ}^3\text{H}^5\text{Ѳ}^2)'$, we also have the right to say that there may be two isomeric residues,

$$\left\{\begin{array}{l} \text{CH}^3 \\ \text{CH}' \\ \left.\begin{array}{l}\text{CO}\\ \text{H}\end{array}\right\}\text{Ѳ} \end{array}\right. \quad \text{and} \quad \left\{\begin{array}{l} \text{CH}^{2\prime} \\ \text{CH}^2 \\ \left.\begin{array}{l}\text{CO}\\ \text{H}\end{array}\right\}\text{Ѳ} \end{array}\right. .$$

One must remember, on the other hand, that the chemical character of an atom depends very much more on the nature, rather than the number of atoms with which it is combined. In effect, the properties of the HѲ residue are closely allied in propyl alcohol and allyl alcohol, even though the quantity of hydrogen in the hydrocarbon radical to which this residue is combined is not the same in the two substances.

By following this line, one will come to the conclusion that six isomeric dibromobutyric acids can exist. By designating as A the group $\left.\begin{array}{l} \text{CO} \\ \text{H} \end{array}\right\}\text{Ѳ}$, these acids will be represented by the following formulas:

$$\text{Ꞓ}^4\text{H}^6\text{Br}^2\text{Ѳ}^2 = \text{Ꞓ}^3\text{H}^5\text{Br}^2\text{A} =$$

I.	II.	III.	IV.
$\left\{\begin{array}{l}\text{CHBr}^2\\ \text{CH}^2\\ \text{CH}^2\text{A}\end{array}\right.$	$\left\{\begin{array}{l}\text{CH}^3\\ \text{CBr}^2\\ \text{CH}^2\text{A}\end{array}\right.$	$\left\{\begin{array}{l}\text{CH}^3\\ \text{CH}^2\\ \text{CBr}^2\text{A}\end{array}\right.$	$\left\{\begin{array}{l}\text{CH}^2\text{Br}\\ \text{CHBr}\\ \text{CH}^2\text{A}\end{array}\right.$

V.	VI.
$\left\{\begin{array}{l}\text{CH}^3\\ \text{CHBr}\\ \text{CHBrA}\end{array}\right.$	$\left\{\begin{array}{l}\text{CH}^2\text{Br}\\ \text{CH}^2\\ \text{CHBrA}\end{array}\right.$

The relationship between the two bromine atoms and the other constituent parts is, as can be seen, different in each one of these formulas, but it is noteworthy that the difference is not of the same kind in the six cases. In formulas I and IV all the bromine is bonded to the

saturated alkyl carbon not combined with the group A; in two other cases, described by formulas V and VI, one brominated carbon atom is bound to a saturated alkyl carbon, and the other brominated carbon atom is bound to the carbonyl carbon (of the group A). The bromine occurs therefore under almost the same influence in cases I and IV as in cases V and VI. As it is not likely that the amount of hydrogen combined to the brominated carbon exerts a marked influence on the chemical character of the bromine atoms, we have the right to expect that bodies I and IV, on the one hand, and bodies V and VI on the other, will be almost identical, and that the number of verifiable isomers of dibromobutyric acids will thus be reduced to four instead of six. I will not insist on the accuracy of these conclusions, but I would suggest that these theoretical considerations are a logical consequence of the principle of chemical constitution, and that, at the same time, the need for the application of this principle, itself generally follows from generally acknowledged ideas about valence and the chemical molecule.

Mr. Kekulé has expressed his considerations of isomerism only briefly; this is why it is difficult to make a positive decision about the meaning of his views. It must be noted, however, from the beginning, that when he speaks of the position of atoms using this term, this chemist means only their chemical bonding in the molecule (the *chemical* structure, or constitution in the sense of the word acknowledged by Mr. Kolbe) [italics mine —DEL]. In effect, it is this bonding and not the position of the atoms in space that is essential to the considerations of Mr. Kekulé. In fact, every speculation with respect to this latter aspect based on chemical reactions would be in direct contradiction with what Mr. Kekulé expresses in his course of organic chemistry (17).

Concerning the structure of succinic acid and its congeners, Mr. Kekulé will undoubtedly acknowledge, as does Mr. Kolbe, that the two $\left.\begin{array}{c}CO \\ H\end{array}\right\}O$ groups that occur in all these substances and are always identical to each other, cannot have any significance for the isomerism. One would be perfectly right, therefore, to acknowledge, with Mr. Kolbe, that the cause of the isomerism of maleic and fumaric acids or of the dibromosuccinic acids must be sought in the isomerism of the C^2H^2 and $C^2H^2Br^2$ groups. But on the other hand, the chemical structure of ethylene, from which these two groups are derived, is not the same according to these two scholars. Mr. Kekulé believes that it is symmetric $\left\{\begin{array}{c}CH'^2 \\ CH^{2\prime}\end{array}\right.$, and that consequently, the 2 free

units of chemical combining power in the substance in question belong to two different carbon atoms, while Mr. Kolbe acknowledges for ethylene the formula

$$\left.\begin{array}{c}CH^3 \\ H\end{array}\right\}C \quad = \quad \left\{\begin{array}{c}CH^3 \\ CH''\end{array}\right.$$
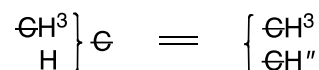
which says the affinity of one of the carbon atoms is completely saturated, and that the two atoms of this element consequently occur in a different chemical state. In effect, the existence of two isomeric bodies

$$\left\{\begin{array}{c}CH^2 \\ CH^2\end{array}\right. \quad \text{and} \quad \left\{\begin{array}{c}CH^3 \\ CH\end{array}\right. \quad = \quad C^2H^4$$
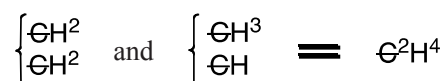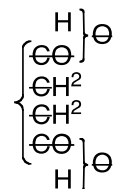
appears to be possible, but there is reason to think that the actual chemical structure of ethylene is described by the first formula, rather than the second. It is known that acetaldehyde contains, in all probability, a methyl group, CH^3, and that the group C^2H^4 (ethylidene of acetaldehyde, which is isomeric and non-identical with olefiant gas) possesses the chemical structure described by the formula $\left\{\begin{array}{c}CH^3 \\ CH\end{array}\right.$ (18). At the s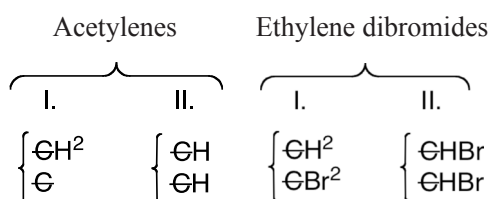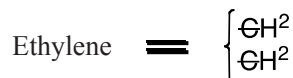ame time, ethylene is formed, as I have shown, when a CH^2 group (methylene) is released. By accepting the formula $\left\{\begin{array}{c}CH^3 \\ CH\end{array}\right.$ for ethylene, one must also accept that for it to be formed, one of the two CH^2 groups loses an atom of hydrogen, and the other gains one, under the same conditions. This is not likely.

Whatever it may be, it is certain that it is actually ethylene that is involved in the composition of succinic acid, and accepting the ideas of Mr. Kekulé with respect to the chemical structure of ethylene, the rational formula of this acid will be

$$\left\{\begin{array}{c}\left.\begin{array}{c}H \\ CO\end{array}\right\}O \\ CH^2 \\ CH^2 \\ \left.\begin{array}{c}CO \\ H\end{array}\right\}O\end{array}\right. .$$

The two saturated alkyl carbon atoms are thus in the same state, therefore it is not clear why the derivatives produced by the elimination of two atoms of hydrogen belonging, on the one hand, to one, and, on the other hand, to the other carbon atom must be isomers and non-identical, as Mr. Kekulé assumes. On the other hand, from the way that that chemist views it, a third isomeric acid must exist: this is the one formed by loss of half the hydrogen from each one of the two saturated alkyl

carbons. Along with Mr. Kolbe, we allow that while keeping the formula $\left\{\begin{array}{l} CH^2 \\ CH^2 \end{array}\right.$ for ethylene, the hydrogen lost or substituted in the formation of maleic and fumaric acids, or in the dibromosuccinic acids comes on the one hand from two, and on the other hand, from a single carbon atom. Thus, we have two acetylenes and two genuine isomeric dibromoethylenes.

$$\text{Ethylene} \quad = \quad \left\{\begin{array}{l} CH^2 \\ CH^2 \end{array}\right.$$

Acetylenes   Ethylene dibromides

I.   II.   I.   II.

$\left\{\begin{array}{l} CH^2 \\ C \end{array}\right.$ $\left\{\begin{array}{l} CH \\ CH \end{array}\right.$ $\left\{\begin{array}{l} CH^2 \\ CBr^2 \end{array}\right.$ $\left\{\begin{array}{l} CHBr \\ CHBr \end{array}\right.$

For the formula $\left\{\begin{array}{l} CH^3 \\ CH \end{array}\right.$ for ethylene, one obtains, as Mr. Kolbe acknowledges, two isomeric acetylenes identical to those whose formulas have just been given, and two dibrominated ethylenes (19).

$\left\{\begin{array}{l} CH^2Br \\ CBr \end{array}\right.$ $\left\{\begin{array}{l} CHBr^2 \\ CH \end{array}\right.$
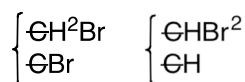
So we see, in brief, that with the one formula for ethylene, as with the other, one comes to analogous results (20). The formula of Mr. Kekulé is more probable, but when one rigorously applies the fundamental principle, the conclusions that Mr. Kolbe comes to appear to be more reasonable (21).

The case of isomerism in the dibrominated pyrotartaric acids and the three aconic acids (mesaconic acid, citraconic acid, and itaconic acid) is not quite analogous to the previous one. In two cases, one is obliged to seek the cause of the isomerism of the acids in the isomerism of the allylene or propylene dibromides. However, if one accepts the chemical structure for propylene described by the formula
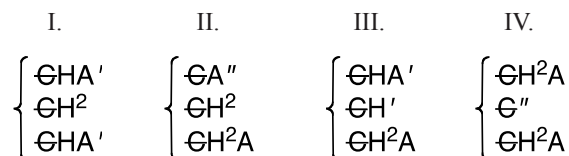
$$\left\{\begin{array}{l} CH'^2 \\ CH^2 \\ CH'^2 \end{array}\right.$$
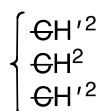
the atoms of this hydrocarbon are not all under the same chemical conditions as are the carbon atoms of ethylene

$\left\{\begin{array}{l} CH'^2 \\ CH'^2 \end{array}\right.$. By again designating the group $\left.\begin{array}{c} CO \\ H \end{array}\right\}O$ by A, the chemical structure of pyrotartaric acid is described by the formula

$$\left\{\begin{array}{l} CH^2A \\ CH^2 \\ CH^2A \end{array}\right.$$
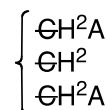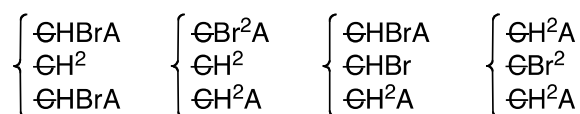
that is to say, in this case two carbon atoms are combined not only with saturated alkyl carbon and hydrogen, but also with a carbonyl carbon, while the third atom of this element is bonded only to alkyl carbon and hydrogen. It thus appears probable that the two substances produced by substitution or elimination of hydrogen belonging to either of the first two carbon atoms are identical to each other, but different from that which is formed when the third group, CH^2, undergoes the same transformation. The point of view of Mr. Kekulé, who thinks that two hydrogen atoms bonded to the same carbon atom are always eliminated or substituted, thus leads us to assume that there are only two cases of isomerism that can exist. But no more than in the case of the derivatives of succinic acid does it explain why the elimination or substitution of hydrogen atoms bonded to different carbon atoms is impossible. On the contrary, acknowledging that the hydrogen eliminated or substituted may equally well come from one carbon atom alone, or two atoms of pyrotartaric acid, one obtains the four following isomers:

Unsaturated acids.

I.   II.   III.   IV.

$\left\{\begin{array}{l} CHA' \\ CH^2 \\ CHA' \end{array}\right.$ $\left\{\begin{array}{l} CA'' \\ CH^2 \\ CH^2A \end{array}\right.$ $\left\{\begin{array}{l} CHA' \\ CH' \\ CH^2A \end{array}\right.$ $\left\{\begin{array}{l} CH^2A \\ C'' \\ CH^2A \end{array}\right.$

Dibrominated acids.

$\left\{\begin{array}{l} CHBrA \\ CH^2 \\ CHBrA \end{array}\right.$ $\left\{\begin{array}{l} CBr^2A \\ CH^2 \\ CH^2A \end{array}\right.$ $\left\{\begin{array}{l} CHBrA \\ CHBr \\ CH^2A \end{array}\right.$ $\left\{\begin{array}{l} CH^2A \\ CBr^2 \\ CH^2A \end{array}\right.$

In the same way, one can form conclusions about the possible isomers for malic and tartaric acids.

If, along with Mr. Kolbe, we describe the chemical structure of propylene by the formula (22)
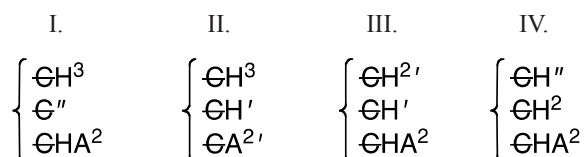
$$\left.\begin{array}{r} C^2H^3 \\ H^2 \end{array}\right\}C^2 \left.\begin{array}{r} \\ H \end{array}\right\} C^2 \quad = \quad \left\{\begin{array}{l} CH^3 \\ CH^2 \\ CH \end{array}\right.$$
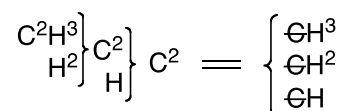
pyrotartaric acid will be described by the formula

$$\left\{\begin{array}{l} CH^3 \\ CH^2 \\ CHA^2 \end{array}\right.$$
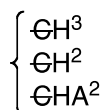
The three carbon atoms in this substance thus occur in different chemical states, but the differences are not the same for each of them. One of the three carbon atoms is bonded to a carbonyl carbon, a saturated alkyl carbon, and to hydrogen; the two others are bonded only to saturated alkyl carbon and hydrogen, but to a different amount of the latter element. One may assume from that, that the latter differences, as noted above, will be less pronounced, and possibly even almost nothing. Whether the differences in the three carbon atoms are acknowledged or not, the conclusions arrived at by Mr. Kolbe appear to be doubtful.

By translating the formulas of Mr. Kolbe, as we have done above, one obtains (23)
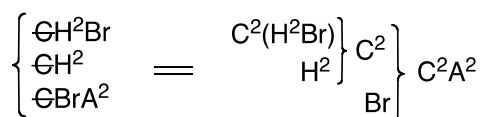
Unsaturated acids.

I.

$$\left\{\begin{array}{l} CH^3 \\ C'' \\ CHA^2 \end{array}\right.$$

II.

$$\left\{\begin{array}{l} CH^3 \\ CH' \\ CA^{2'} \end{array}\right.$$

III.

$$\left\{\begin{array}{l} CH^{2'} \\ CH' \\ CHA^2 \end{array}\right.$$

IV.

$$\left\{\begin{array}{l} CH'' \\ CH^2 \\ CHA^2 \end{array}\right.$$

Dibrominated acids.

$$\left\{\begin{array}{l} CH^3 \\ CBr^2 \\ CHA^2 \end{array}\right. \quad \left\{\begin{array}{l} CH^3 \\ CHBr \\ CBrA^2 \end{array}\right. \quad \left\{\begin{array}{l} CH^2Br \\ CHBr \\ CHA^2 \end{array}\right. \quad \left\{\begin{array}{l} CHBr^2 \\ CH^2 \\ CHA^2 \end{array}\right.$$
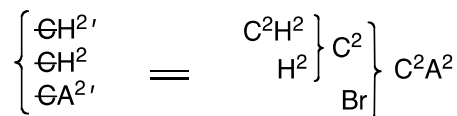
It is apparent therefore that the substances whose chemical structures are described by formulas III and IV are almost identical if the character of the two carbon atoms, which only differ in the *quantity* of hydrogen to which they are bound, is the same. In effect, the bromine or the free affinity belonging to saturated alkyl carbon atoms not bounded to group A in bodies (III) and (IV) only differ in the degree of hydrogenation.

Should one want to acknowledge preferably that the three atoms of propylene are different, one must conceive of the possibility of the existence of not four, as Mr. Kolbe assumes, but five isomeric acids. In fact, besides the four cases pointed out by this chemist, the following case must also have a place:

Notation of Mr. Kolbe (24)

$$\left\{\begin{array}{l} CH^2Br \\ CH^2 \\ CBrA^2 \end{array}\right. \quad = \quad \left.\begin{array}{l} C^2(H^2Br) \\ H^2 \\ Br \end{array}\right\}C^2 \Big\} C^2A^2$$

Notation of Mr. Kolbe

$$\left\{\begin{array}{l} CH^{2'} \\ CH^2 \\ CA^{2'} \end{array}\right. \quad = \quad \left.\begin{array}{l} C^2H^2 \\ H^2 \\ Br \end{array}\right\}C^2 \Big\} C^2A^2$$
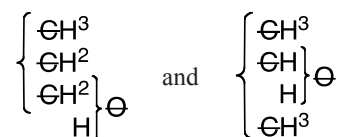
The bodies described by these formulas are no less different from the preceding ones than those are from each other. In addition, there is no reason why this fifth case should be contradictory to Mr. Kolbe's views because the only difference between the formulas that describe it [the fifth isomer —DEL] and some of this scholar's other formulas being the place that is occupied by an atom of bromine or a free affinity. For example:
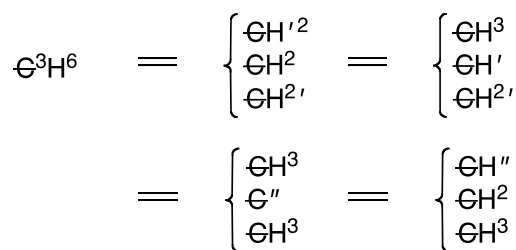
Formula of the fifth case.
Notation of Mr. Kolbe.

$$\left.\begin{array}{l} C^2(H^2Br) \\ H \\ H \end{array}\right\}C^2 \Big\} C^2 \quad \text{...Br}$$

Formula of the third case.
Notation of Mr. Kolbe (25).

$$\left.\begin{array}{l} C^2(H^2Br) \\ H \\ Br \end{array}\right\}C^2 \Big\} C^2 \quad \text{...H}$$
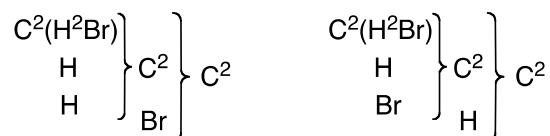
Mr. Kolbe tries to explain the isomerism of propyl alcohols by deriving their formulas by substitution. It should be noted here, as everywhere else, that the rigorous application of the principle of chemical structure appears to provide a better method to estimate the true scope of these speculations. This principle, like the preceding substitution used by Mr. Kolbe, permits the prediction of two isomeric alcohols.

$$\left\{\begin{array}{l} CH^3 \\ CH^2 \\ CH^2 \\ H \end{array}\right\}O \quad \text{and} \quad \left\{\begin{array}{l} CH^3 \\ CH \\ H \\ CH^3 \end{array}\right\}O$$

The first of these formulas is the one that Mr. Kolbe gives to normal propyl alcohol; the second corresponds to the alcohol obtained by hydrogenation of acetone. The same principle leads to the assumption that four isomeric propylenes exist:

$$C^3H^6 \quad = \quad \left\{\begin{array}{l} CH'^2 \\ CH^2 \\ CH^{2'} \end{array}\right. \quad = \quad \left\{\begin{array}{l} CH^3 \\ CH' \\ CH^{2'} \end{array}\right.$$

$$= \quad \left\{\begin{array}{l} CH^3 \\ C'' \\ CH^3 \end{array}\right. \quad = \quad \left\{\begin{array}{l} CH'' \\ CH^2 \\ CH^3 \end{array}\right.$$

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The first two, whose carbon atoms differ only in the amount of hydrogen to which they are bonded, are probably closer to each other than to the third, which contains a carbon atom without any hydrogen, and the fourth will perhaps be almost identical to the second.

One runs the risk of coming to unlikely conclusions, if, losing sight of the chemical structure of the bodies that react and that of the bodies produced, one speculates on the relationships that exist between their composition and the composition of other substances. As an instructive example, we may cite the considerations of Mr. Kolbe on the di- and tri-glycolamidic acids (26) obtained by Mr. Heintz. Regarding the formation of glycine and these interesting bodies, there is nothing simpler than the following: their formation is perfectly analogous to the formation of methylamine, and di- and tri-methylamine, when these bases are obtained by the action of methyl bromide on ammonia. In all these cases, the reaction consists of a simple double decomposition where the monovalent residue, formed by loss of a halogen atom from the organic molecule, binds with the ammonia residue. Since the nitrogen of the ammonia acts with three units of chemical combining power, it is possible to form three species in which one atom of the residue and two atoms of hydrogen, or two atoms of the residue and one atom of hydrogen, or eventually three atoms of the residue, are bound in one molecule by the affinity of nitrogen. In the case of the formation of Mr. Heintz's acids, the organic residue is:

$$(\mathrm{C^2H^3O^2})' \;=\; \mathrm{C^2H^3ClO^2} \;-\; Cl \;=\; \left\{ \begin{array}{l} (\mathrm{CH^2})' \\ \mathrm{CO} \\ \quad\; H \end{array} \right\} O \,.$$
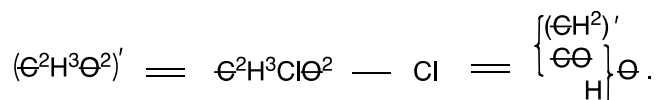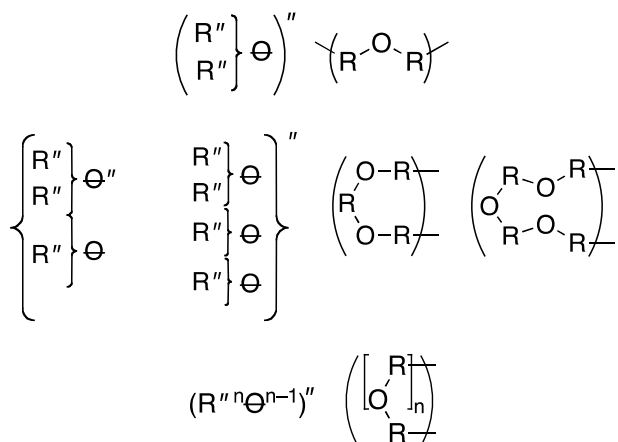
After that, it is entirely superfluous to accept the production of an unsaturated molecule (monochloroacetic acid *less* hydrogen chloride), as does Mr. Kolbe, and we easily envisage that with concentrated ammonia, the primary product is formed, and with dilute ammonia the secondary and tertiary products are formed predominantly. It becomes evident, at the same time, that diglycolamidic acid corresponds to aspartic acid as does dimethylamine to ethylamine, which is to say that here exists a genuine *metamerism*. In the molecule of aspartic acid, as in those of succinic, malic and other acids, and in ethylamine, all the carbon atoms are directly bonded to each other. In the molecule of the di- and triglycolamidic acids, as in that of di- and trimethylamine, they are only bonded through the nitrogen atom acting through its three units of chemical combining power.

The facts demonstrate that, in general, atoms or groups bonded indirectly in a molecule through other intermediate atoms, split apart when the latter atoms are lost. This is the way, for example, that alcohol radicals, held together in ethers by the divalent oxygen atom, split apart by the action of phosphorus iodide, and one obtains two molecules of the organic iodide from one molecule of ether because the divalent oxygen is replaced by iodine, whose atoms, because of their monovalency, cannot serve to join two or more other atoms. Following these guidelines, we can positively assume that the polyglycolamidic acids of Mr. Heintz will split into molecules containing only $\mathrm{C^2}$ (probably glycolic acid), once their nitrogen is removed by the action of hyponitric acid.

It is more likely, Mr. Wurtz assumes, that diglycolic acid will result from the action of nitrous acid on diglycolamidic acid. In that case, the units of chemical combining power belonging to the organic residues will be saturated at the moment of reaction, not separately by HO residues, as it should be during the formation of glycolic acid, but both together by an oxygen atom. However, to accept such a metamorphosis (in the presence of water), it would be necessary to observe an analogous reaction for triglycolamidic acid, and to me, this seems to present some difficulties. In fact, I think that there must exist a diglycolamidic acid metameric with that of Mr. Heintz, and that will be to diglycolic acid as glycine is to diglycolic acid, and that will give the latter by the action of nitrous acid. These ideas, which lead me to this assumption, and that are derived from the principle of chemical structure, may be able to clarify, to a certain point, some questions concerning the nature of polyacids, polyalcohols, and their congeners. It is known that the elegant research of Mr. Wurtz has shown that ethylene oxide, on reacting with ammonia, gives rise to a series of oxygenated bases, some of which contain in their molecule more than four atoms of ethylene. This latter circumstance would seem, at first, to prevent us envisaging these interesting compounds as derivatives of the ammonia type formed by substitution, but it can be explained as will be found below.

The composition of polyacids and polyalcohols shows a characteristic property: each time the divalent radical enters into their molecule, it also introduces an atom of oxygen. From that, it is natural to assume that it is this latter element that effects the bonding of the radicals. Indeed, it is easy to understand that two, three, four, or several divalent atoms or groups can, by bonding with each other, produce another divalent group. Thus, a divalent radical R" and oxygen can give the following series (27):

$$\left(\begin{matrix} R'' \\ R'' \end{matrix}\right\} \ominus \right)'' \qquad \left(R \diagup^{O} \diagdown R\right)$$

$$\left\{\begin{matrix} R'' \\ R'' \\ R'' \end{matrix}\right\} \ominus'' \qquad \left[\begin{matrix} R'' \\ R'' \\ R'' \\ R'' \end{matrix}\right\} \ominus \right]'' \qquad \left(R\left\langle \begin{matrix} O-R \\ O-R \end{matrix}\right\rangle\right) \qquad \left(\begin{matrix} R\diagdown_{O}\diagup^{R} \\ O\diagup \diagdown_{R}\diagdown_{O}\diagdown_{R} \end{matrix}\right)$$

$$(R''^{n}\ominus^{n-1})'' \qquad \left(\left[O\diagup^{R}\right]_{n} R\right)$$

Again, there is an analogous case, when methylene doubles [dimerizes], triples [trimerizes], and so on, in forming homologous hydrocarbons.

$$CH^{2} \quad \left\{\begin{matrix} CH^{2} \\ CH^{2} \end{matrix}\right. \quad \left\{\begin{matrix} CH^{2} \\ CH^{2} \\ CH^{2} \end{matrix}\right. \quad \cdots\cdots \quad \left[n(CH^{2})\right]'' \quad = \quad (C^{n}H^{2n})''$$
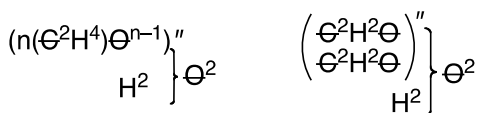
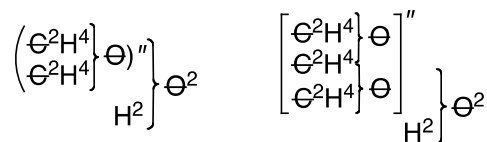The general formula of the polyalcohols and polyacids, like those of ordinary alcohols and dibasic acids will

thus be $\left.\begin{matrix} R'' \\ H^{2} \end{matrix}\right\} \ominus^{2}$ and the difference will only consist of the meaning of R'', which for the alcohols is $R^{n}O^{n-1}$.

Thus, one obtains, for example, the following formulas describing the chemical structure of the bodies.
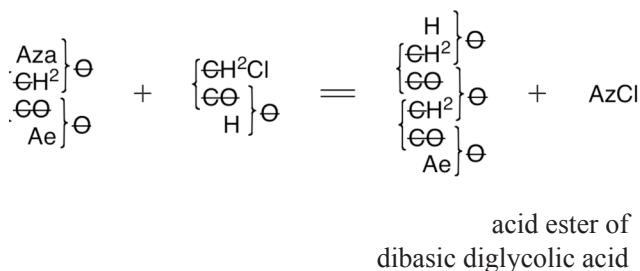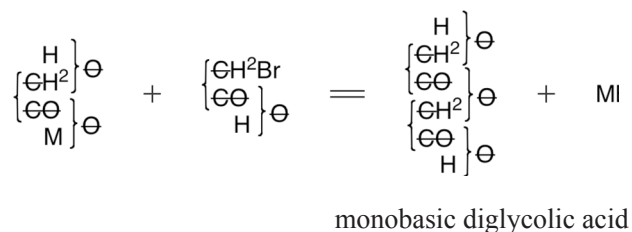
ethylenic alcohol

$$\left.\begin{matrix} (n(C^{2}H^{4})\ominus^{n-1})'' \\ H^{2} \end{matrix}\right\}\ominus^{2}$$

diglycolic alcohol

$$\left.\left(\begin{matrix} C^{2}H^{2}\ominus \\ C^{2}H^{2}\ominus \end{matrix}\right)''\right\}\ominus^{2}$$
$$H^{2}$$

diethylenic alcohol

$$\left.\left(\begin{matrix} C^{2}H^{4} \\ C^{2}H^{4} \end{matrix}\right\}\ominus)''\right\}\ominus^{2}$$
$$H^{2}$$

triethylenic alcohol

$$\left.\left[\begin{matrix} C^{2}H^{4} \\ C^{2}H^{4} \\ C^{2}H^{4} \end{matrix}\right\}\begin{matrix}\ominus \\ \ominus \\ \ominus\end{matrix}\right]''\right\}\ominus^{2}$$
$$H^{2}$$

This perspective leads to the assumption that two isomeric diglycolic acids exist, of which one contains two acidic H$\ominus$ residues (bonded to carbonyl carbons), and the other one acidic H$\ominus$ residue and one alcoholic H$\ominus$ residue (combined with a saturated alkyl carbon). The second acid would have to be formed by the action of monochloroacetic acid on glycolates but since, in Mr. Heintz' experience, this reaction does not succeed, perhaps it can be obtained by the double decomposition of monobromoacetic acid or monoiodoacetic acid with glycolates. The first, already known, diglycolic acid can

doubtlessly be made in the from of the ester by the action of monochlorinated (monobrominated, monoiodinated) acetic acid on neutral monoethyl glycolate, in which the hydrogen of the alcoholic H$\ominus$ residue is replaced by sodium. The following formulas describe these reactions and the chemical structure of the two diglycolic acids (28).

$$\left.\begin{matrix} H \\ CH^{2} \\ CO \\ M \end{matrix}\right\}\begin{matrix} \\ \ominus \\ \ominus \end{matrix} \quad + \quad \left.\begin{matrix} CH^{2}Br \\ CO \\ H \end{matrix}\right\}\begin{matrix} \\ \ominus \end{matrix} \quad = \quad \left.\begin{matrix} H \\ CH^{2} \\ CO \\ CH^{2} \\ CO \\ H \end{matrix}\right\}\begin{matrix} \ominus \\ \\ \ominus \\ \\ \ominus \end{matrix} \quad + \quad MI$$

monobasic diglycolic acid

$$\left.\begin{matrix} Aza \\ CH^{2} \\ CO \\ Ae \end{matrix}\right\}\begin{matrix} \\ \ominus \\ \\ \ominus \end{matrix} \quad + \quad \left.\begin{matrix} CH^{2}Cl \\ CO \\ H \end{matrix}\right\}\begin{matrix} \\ \ominus \end{matrix} \quad = \quad \left.\begin{matrix} H \\ CH^{2} \\ CO \\ CH^{2} \\ CO \\ Ae \end{matrix}\right\}\begin{matrix} \ominus \\ \\ \ominus \\ \\ \ominus \end{matrix} \quad + \quad AzCl$$
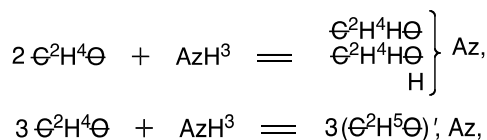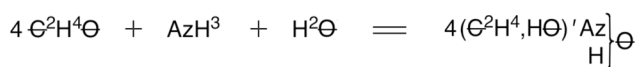
acid ester of
dibasic diglycolic acid

It is clear that the divalent compound radical $(R^{n})''(O^{n-1})''$ acts in most cases like a simple divalent radical, and can also give derivatives of the ammonia type. It is also known that a divalent group becomes monovalent itself when it bonds to a monovalent group. This explains the formation of Mr. Wurtz' oxygenated bases and leads to the assumption of a crowd of isomeric compounds. In the reaction of ethylene oxide and ammonia, the hydrogen of the latter substance combines with the oxygen of the former, forming the H$\ominus$ residue, and this, on bonding to divalent ethylene, gives the monovalent ethyl oxide $(C^{2}H^{5}\ominus)'$, which remains bonded to the ammoniacal residue, producing the base

$$C^{2}H^{4}\ominus \quad + \quad AzH^{3} \quad = \quad \left.\begin{matrix} C^{2}H^{4'}H\ominus' \\ H \\ H \end{matrix}\right\} Az$$
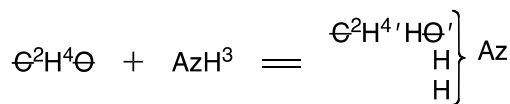
As far as the presence of the hydroxyl hydrogen (of the residue H$\ominus$) in these bases is concerned, that has been put beyond doubt by the research of Mr. A. Hofmann.

The formation of secondary and tertiary amines, etc., is therefore explained in a completely analogous way (29).

$$2\,C^{2}H^{4}\ominus \quad + \quad AzH^{3} \quad = \quad \left.\begin{matrix} C^{2}H^{4}H\ominus \\ C^{2}H^{4}H\ominus \\ H \end{matrix}\right\} Az,$$

$$3\,C^{2}H^{4}\ominus \quad + \quad AzH^{3} \quad = \quad 3(C^{2}H^{5}\ominus)', Az,$$

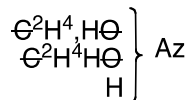$$4\,C^2H^4O \;+\; AzH^3 \;+\; H^2O \;=\; 4\,(C^2H^4,HO)'Az \Big]_{H} O$$

In every case, the carbon groups are bonded into a single molecule by the chemical combining power of the nitrogen, but they can also, as seen above, be bonded
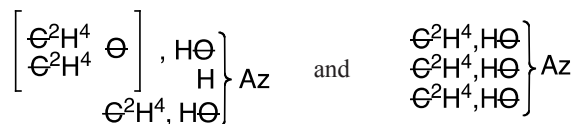
$$\left[\begin{array}{c} C^2H^4 \\ C^2H^4 \end{array}\right]O \left.\begin{array}{c} HO \\ H \\ H \end{array}\right\} Az$$
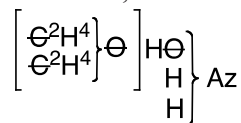
through oxygen. Thus, an amine , metameric with the amine

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

must also exist. The second of these bases is the secondary amine (an imide base) from glycol when it acts as a monoatomic alcohol

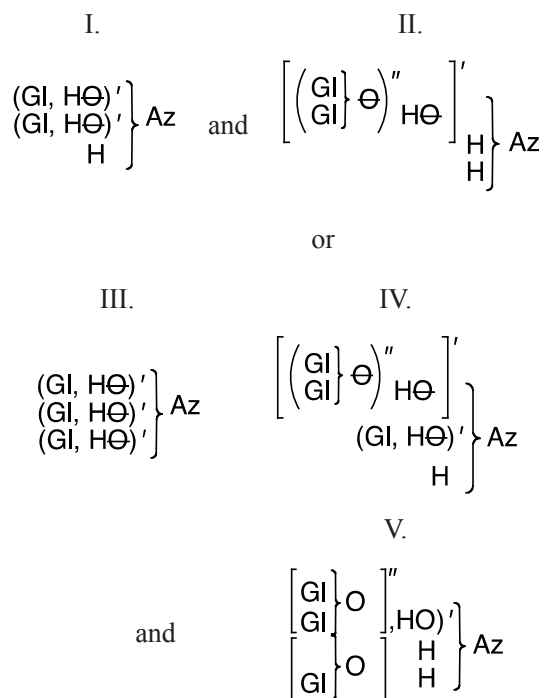$$\left.\begin{array}{c} (C^2H^4,HO)' \\ H \end{array}\right\}O$$
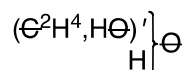
while the first is the primary amine from diethylene alcohol. Likewise, the following two metameric substances must also exist:

$$\left[\begin{array}{c} C^2H^4 \\ C^2H^4 \end{array}O\right],\left.\begin{array}{c} HO \\ H \\ C^2H^4,HO \end{array}\right\}Az \quad \text{and} \quad \left.\begin{array}{c} C^2H^4,HO \\ C^2H^4,HO \\ C^2H^4,HO \end{array}\right\}Az$$

The subsequent application of this view is easy, and the isomeric amines that appear in limitless number are distinguished from each other by the amount of hydrogen directly bonded to the nitrogen (ammonia-type hydrogen). One should be able to easily recognize their nature by preparing, for example, their methyl derivatives. The HO residue in the alcohol cannot be substituted by the direct action of the iodide—that is beyond doubt. It can probably be replaced by means of an indirect method, by substituting sodium for the hydrogen of the residue, and treating the sodium alkoxide with the iodide. It can equally well be replaced by the reaction of a sodium alkoxide with a derivative of the base containing a halogen group in place of the HO residue whose hydrogen one wants to replace.

The polyamide acids should give similar results. Designating the glycolyl radical (C^2H^2O) (30) by Gl, for example, one obtains the following metameric species:

I.

$$\left.\begin{array}{c} (Gl,HO)' \\ (Gl,HO)' \\ H \end{array}\right\}Az \quad \text{and}$$

II.

$$\left[\left(\begin{array}{c} Gl \\ Gl \end{array}O\right)''HO\right]'\left.\begin{array}{c} \\ H \\ H \end{array}\right\}Az$$

or

III.

$$\left.\begin{array}{c} (Gl,HO)' \\ (Gl,HO)' \\ (Gl,HO)' \end{array}\right\}Az$$

IV.

$$\left[\left(\begin{array}{c} Gl \\ Gl \end{array}O\right)''HO\right]'\left.\begin{array}{c} \\ (Gl,HO)' \\ H \end{array}\right\}Az$$

V.

$$\left[\begin{array}{c} Gl \\ Gl \end{array}O\right]''\left.\begin{array}{c} ,HO)' \\ H \\ H \end{array}\right\}Az$$
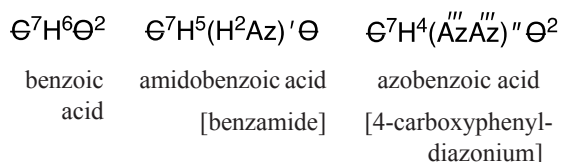
Formulas (I) and (III) represent the di- and tri-amidic acids of Mr. Heintz, which are, in all probability, secondary and tertiary monoamines. Formulas (II and V) belong to the class of primary amines, which are to diglycolic and triglycolic acid as glycine is to glycolic acid. Finally, the amide acid described by the formula (IV) is a secondary amine containing a compound residue of diglycolic acid and a simple glycolic acid residue. By the action of nitrous acid, this last compound would possibly give diglycolic acid and glycolic acid at the same time.

May these considerations lead to experiments in the direction that they indicate!
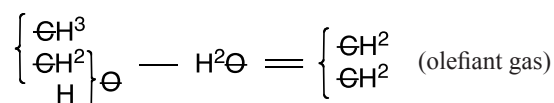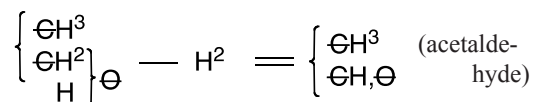
References and Notes

1. Kolbe, *Lehrbuch*, vol. 1, p. 23.

2. Gerhardt, *Traité*, vol. IV, p. 561.

3. Kekulé, *Lehrbuch*, vol. I, p. 61.

4. Kolbe, *Lehrbuch*, vol. I, p. 13. See also vol. II, p. 576.

5. Gerhardt, *Traité*, vol. IV, p. 573.

6. Kekulé, *Lehrbuch*, vol. 1, p. 157.

7. Kekulé, *Lehrbuch*, vol. I, p. 164 and 161; see also vol. II, p. 6 and 7.

8. This word already appears to describe the position of the atoms in space, which is in contradiction to the ideas that one finds a little earlier in the same work (vol. I, p. 157 and 162).

9. *The topographical position of the atoms*, an expression that has also been used lately, appears to me to be less suitable because it implies the idea of determining the position of the atoms in space. Speaking of the ratio of the atoms in a molecule, one need not know their positions, nor even admit the existence of physical atoms. Only in the case where the hypothesis of the existence of these last would be absolutely necessary for a chemist, would one have the right to assert that the considerations of Mr. Kolbe constitute an attempt to determine the position of the atoms in space. Since the hypothesis of physical atoms has not yet become essential for our science, and since certain chemists do not admit the possibility of determining their position, each expression that implies this hypothesis and this possibility will only delay the time when the different theoretical views will be merged into one.

10. Kekulé, *Lehrbuch*, vol. I, p. 158.

11. Kekulé, *Lehrbuch*, vol. I, p. 177; vol. I, p, 95 and 96.

12. Kekulé, *Lehrbuch*, vol. I, p. 556.

13. [The carbon is shown here with a bar, presumably as Butlerov intended. In the original, the bar is missing, presumably a printing error. —DEL]

14. Kekulé, *Lehrbuch*, vol. II, p. 2.

15. Kolbe, *Lehrbuch*, vol. I, p. 742.

16. This perspective has led Mr. Kolbe to express opinions that will never be reconciled with theoretical ideas of valence. In his paper on the isomerism of fumaric and maleic acids, etc., for example, he notes that carbon is not only a di- and tetravalent atom, but also trivalent. He views the composition of oxalic acid, $2OH,C^4O^6$, as a proof of this trivalency. He loses sight of the reason why the two carbon atoms (the two carbonyls of Mr. Kolbe) are linked together, and which is certainly nothing other than the action of a quarter of the chemical combining power belonging to each atom of that element, and holding these atoms [together] not only in oxalic acid, but also in ethyl hydride, alcohol, glycol, etc. It is certainly correct to state that the carbon group $2C^{IV}$ is hexavalent, but not to deduce from that that the carbon itself is a trivalent atom. By rigorously following Mr. Kolbe's view, one would have to accept that carbon has a valence of 2 2/3 in mesoxalic acid and propyl hydride, of 2 1/2 in butyl hydride, monovalent in phenyl hydride, and so forth. It should be pointed out at the same time, that Mr. Kolbe's idea on the state of nitrogen in Mr. Griess' substances is not new to me. More than a year ago, I expressed it in my paper, "On amines," (in the Russian language, in the writings of Kazan University). There I gave the following parallel:

$$C^7H^6O^2 \qquad C^7H^5(H^2Az)'O \qquad C^7H^4(\overset{'''}{Az}\overset{'''}{Az})''O^2$$

benzoic   amidobenzoic acid   azobenzoic acid
acid
          [benzamide]   [4-carboxyphenyl-
   diazonium]

and I pointed out the way in which the substances in question form, which consists of the substitution of an atom of nitrogen by three atoms of hydrogen (of which two are bonded to the nitrogen), and gives some probability to this hypothesis.
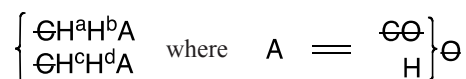
17. Vol. I, p. 157.

18. The formation of ethylene and ethylidene oxide (acetaldehyde) can be explained by the loss of hydrogen atoms belonging to different carbon atoms in alcohol.
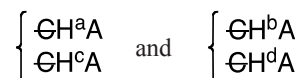
$$\left.\begin{array}{c} CH^3 \\ CH^2 \\ H \end{array}\right\}O \;-\; H^2 \;=\; \left\{\begin{array}{l} CH^3 \\ CH,O \end{array}\right. \quad \begin{array}{l}(\text{acetalde-} \\ \text{hyde})\end{array}$$

$$\left.\begin{array}{c} CH^3 \\ CH^2 \\ H \end{array}\right\}O \;-\; H^2O \;=\; \left\{\begin{array}{l} CH^2 \\ CH^2 \end{array}\right. \quad (\text{olefiant gas})$$

19. [The first of these structures has an extra hydrogen atom in the original, appearing as

$$\left\{\begin{array}{l} CH^2Br \\ CHBr \end{array}\right. \; . \text{ —DEL]}$$
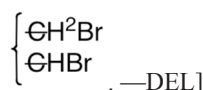
20. [Butlerov's logic here predicts that both the Kekulé and Kolbe structures will give two isomeric dibromides, but it is equally clear that they do not predict the same two structures. Here, Butlerov does not appear to be willing to endorse one set of structures over the other—perhaps because he could not deduce a method to distinguish between them. —DEL]

21. I find it difficult to understand why Mr. Erlenmeyer accepts that the hydrogen lost from succinic acid comes from each of two different carbon atoms (*Zeitschrift für Chemie und Pharmacie*, **1863**, p. 22). This point of view assumes that the hydrogen contained in ethylene are different; if all four hydrogen atoms of olefiant gas were different, one would have to have 4 isomers $C^4H^4O^4$. Indeed, if succinic acid is expressed by the formula

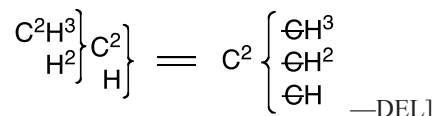$$\left.\begin{array}{l} CH^aH^bA \\ CH^cH^dA \end{array}\right\} \quad \text{where} \quad A = \left.\begin{array}{c} CO \\ H \end{array}\right\}O$$

one can clearly see that the bodies

$$\left\{\begin{array}{l} CH^aA \\ CH^cA \end{array}\right. \quad \text{and} \quad \left\{\begin{array}{l} CH^bA \\ CH^dA \end{array}\right.$$
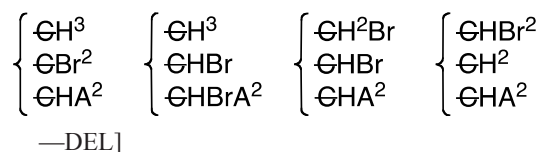
must be identical if all the hydrogen atoms are identical, and that it is possible for 4 isomers of $C^4H^4O^4$ to exist if

all the atoms of this element are different.

22. [There is clearly an error in this formula, with the "C²" and "=" symbols being transposed. The corrected version has been used in the translation. The original publication contains the following:

$$\left.\begin{array}{l}C^2H^3\\H^2\end{array}\right\}\left.\begin{array}{l}C^2\\H\end{array}\right\} \;\;=\;\; C^2\left\{\begin{array}{l}\text{C̶H}^3\\\text{C̶H}^2\\\text{C̶H}\end{array}\right. \qquad \text{—DEL]}$$

23. [There are clearly errors in the left-hand pair of acids, with the second structure containing a formally pentavalent carbon. The corrected version of the set has been used in the translation. The original publication contains the following:

$$\left\{\begin{array}{l}\text{C̶H}^3\\\text{C̶Br}^2\\\text{C̶HA}^2\end{array}\right.\quad\left\{\begin{array}{l}\text{C̶H}^3\\\text{C̶HBr}\\\text{C̶HBrA}^2\end{array}\right.\quad\left\{\begin{array}{l}\text{C̶H}^2Br\\\text{C̶HBr}\\\text{C̶HA}^2\end{array}\right.\quad\left\{\begin{array}{l}\text{C̶HBr}^2\\\text{C̶H}^2\\\text{C̶HA}^2\end{array}\right.$$

     —DEL]

24. [The printed version places the dibrominated and unsaturated acid structures on the same line in such a way that it is not clear that there are two separate structures. In addition, the dibrominated structure, shown below,

includes a barred carbon atom (C), which is not part of Kolbe's notation:

$$\left.\begin{array}{l}\text{C̶}^2(H^2Br)\\H^2\end{array}\right\}C^2\left.\begin{array}{l}\\\\Br\end{array}\right\}C^2A^2$$

     — DEL]
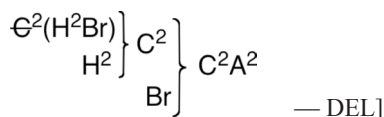
25. *Lehrbuch*, Vol. II, p. 587.

26. [These compounds are known today as nitrilodiacetic acid, and nitrilotrioacetic acid, respectively. —DEL]

27. [The structures on the right are "translations" of Butlerov's structures into modern notation. —DEL]

28. If I use these types of formulas here and above to describe the chemical structure, it is because these formulas resemble the type formulas to which we are generally accustomed.

29. [The first of these structures was misprinted in the original, as shown below; the oxygens in the product were not barred.

$$2\;\text{C̶}^2H^4\text{O̶} \;+\; AzH^3 \;\;==\;\; \left.\begin{array}{l}\text{C̶}^2H^4HO\\\text{C̶}^2H^4HO\\H\end{array}\right\}Az$$
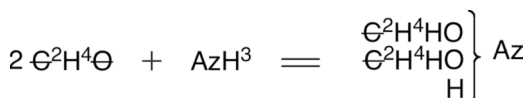
     —DEL]

30. [This corresponds to the modern structure –CH₂CO–. —DEL]

Outstanding Paper Award 2014

HIST has named the recipient of its Outstanding Paper Award for 2014: Amy Bix in the History Department at Iowa State University. The award is presented to the author of the best paper published in the Bulletin for the History of Chemistry during the previous three years. In this instance, papers published in 2012, 2013 and 2014 were considered. Bix's paper, entitled "Chemistry of Cooking, Chemistry in War: Women in Nineteenth and Twentieth-Century Land-Grant Science and Engineering," appeared in volume 38(2) of the Bulletin, in an issue devoted largely to the 150th anniversary of the Land-Grant Colleges Act in the USA (commonly known as the Morrill Act).