On the classification of chemical substances by means of generic radicals / by Alexander Crum Brown.

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ON THE

CLASSIFICATION OF CHEMICAL SUBSTANCES,

BY MEANS OF

GENERIC RADICALS.

BY

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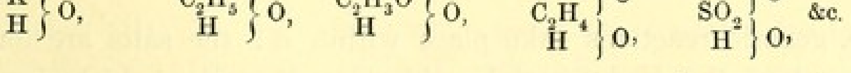
XXV.—*On the Classification of Chemical Substances, by means of Generic Radicals*. By Alexander Crum Brown, M.D., D.Sc.

(Read 5th February 1866.)

The idea of chemical structure, as founded on that of atomicity (or the equivalence of atoms), enables us to divide any molecule, whose chemical structure is known, into radicals. The number of ways in which this may be done increases with the complexity of the molecule. Each of these modes of division corresponds to a series of conceivable reactions, some of which have been observed. Any one of these series may be made the basis of classification; but it is obviously most convenient to select for this purpose the most characteristic reactions, and those which are common to such substances as form natural groups. In studying these, we find that each series implies the presence of a particular radical, within which the reactions in question take place. We may call such series of reactions the Generic reactions, and the corresponding radicals Generic radicals. These are sometimes residues of double decomposition, but very frequently this is not the case, and this may account for the fact, that the importance of these generic radicals has been very much overlooked.

I shall consider some of the cases in which this principle of classification is already, to some extent, recognised, before proceeding to apply it generally, and examine first those examples furnished by groups of bodies which are referred to the types H_2O and NH_3.

I. A large number of the substances referred to the type H_2O, are formed by the replacement of *one* atom of H in each molecule of H_2O, by a radical, as,—



$$\left.\begin{array}{c}K\\H\end{array}\right\}O,\qquad \left.\begin{array}{c}C_2H_5\\H\end{array}\right\}O,\quad \left.\begin{array}{c}C_2H_3O\\H\end{array}\right\}O,\qquad \begin{array}{c}H\\C_2H_4\\H\end{array}\begin{array}{l}\}\,O\\ \}\,O,\end{array}\qquad \begin{array}{c}H\\SO_2\\H\end{array}\begin{array}{l}\}\,O\\ \}\,O,\end{array}\quad \&c.$$

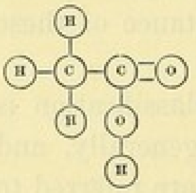
The part common to all such bodies is the radical $(HO)'$ or $\left.\begin{array}{c}\cdot\\H\end{array}\right\}O$, and the reactions common to the group affect this radical alone. These reactions are—1*st*, The replacement of $(HO)'$; 2*d*, The replacement of H in $(HO)'$; and 3*d*, The replacement of O in $(HO)'$. Thus (HO) may be replaced by Cl, Br, &c., or $(HO)_2$ by O; $(HO)'$ may become $(KO)'$, $(C_2H_5O)'$, &c. by the replacement of H, or (HS), $(HSO_4)'$, &c. by replacement of O. $(HO)'$ is therefore the generic radical of this large genus.

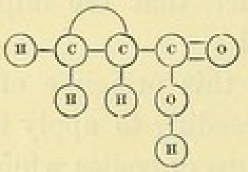
II. An extensive series of substances referrible to the type NH_3 have only *one* atom of H in each molecule of ammonia replaced.

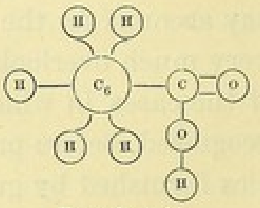
As $$\left.\begin{matrix}C_2H_5\\H_2\end{matrix}\right\}N,\quad \left.\begin{matrix}C_2H_3O\\H_2\end{matrix}\right\}N,\quad \left.\begin{matrix}C_2H_3O_2\\H_2\end{matrix}\right\}N,\quad \begin{matrix}H_2\\C_2H_4\\H_2\end{matrix}\begin{matrix}\}N\\ \\ \}N\end{matrix}\quad \begin{matrix}H_2\\C_2O_2\\H_2\end{matrix}\begin{matrix}\}N,\\ \\ \}N,\end{matrix}\quad \&c.$$

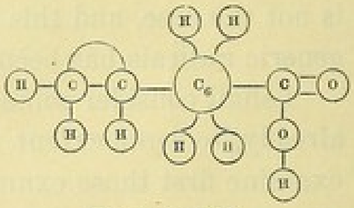
In these we have $(NH_2)'$, or $\left.\begin{matrix}\dot{}\\H_2\end{matrix}\right\}N$ common to the group. The generic reactions are—1*st*, Replacement of one or both atoms of H in NH_2 by radicals. 2*d*, The addition of two monatomic atoms to each NH_2, N''' becoming N^v. 3*d*, The replacement of N''' by O'' and $(HO)'$ (by the action of nitrous acid), or what comes to the same thing, the replacement of NH_2 by HO. All these affect the radical NH_2 alone, which is therefore the generic radical. In the same way $(NH)''$ is the generic radical of the substances derived from ammonia, by the replacement of two atoms of H.

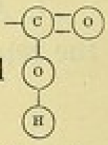
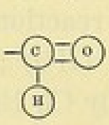
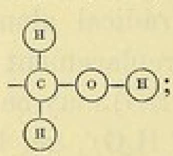
The best way of extending this method of classification generally, is to examine the chemical structure of those bodies which form well-marked genera, and see what group of atoms they have in common, and whether the common group (or radical) is that part of the molecule, in which the reactions characteristic of the genus take place. One very well-marked genus is that of the monobasic acids, which have aldehydes and alcohols corresponding to them (KOLBE's "Monocarbonsäuren"). As examples, we may take acetic acid, acrylic acid, benzoic acid, and cinnamic acid. The chemical structure of these substances is represented, as far as known, by the following graphic formulæ :—


Acetic Acid.

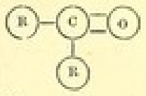

Acrylic Acid.


Benzoic Acid.

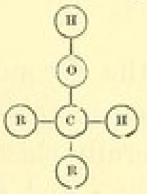

Cinnamic Acid.

The part common to all these acids is obviously the monatomic radical  and the generic reactions take place within it ; the salts are formed by the replacement of the H by metal,—chlorides, bromides, aldehydes, &c., by the replacement of the (HO)', by Cl, Br, H, &c. ; alcohols from the aldehydes, by the addition of H_2  becoming ; amides, by the replacement of (HO)' by NH_2; nitriles, by the replacement of O'' and $(HO)'$ by N''' ; acetones, from two molecules, by the loss of CO(HO) in one, and the substitution of the radical thus produced for HO in the other. $\{(CO(HO)\}'$ is, then, the generic radical of these acids. As this radical is of very great importance, it is advisible to indicate it by a single symbol, and I shall use the Greek letter Ξ for this purpose.* The relation of Ξ to CN, or of the acid to the nitrile, is seen not only in the monobasic acids (monocarbonsäuren), but also in the di- and tri-basic acids (di- and tricarbonsäuren), so that these contain the radical Ξ, two and three times respectively.

The investigation sketched above also shows that COH and $CH_2(HO)$, are the radicals of the aldehydes and the "true" alcohols. Pursuing this method further, we arrive at a system of classification for the various groups of pseudo-alcohols, the number of which has recently increased so much. One of these groups is formed by the hydrogenation of the acetones. The acetones have the general formula COR_2 (in which R_2 may represent either two atoms of the same or of two different radicals); taking the graphic formula, we have



( being the generic radical), by the addition of H_2, we get



the reaction being similar to that by which the aldehydes are converted into true alcohols, one of the two pairs of equivalents by which the O atom is united to the C, being separated, and hydrogen added to each of the equivalents (one of O and one of C), thus rendered free. The generic radical here is obviously $\{(CH(HO)\}''$, and the subgenera and individual substances are determined by the radicals saturating the two free equivalents of this generic radical. This genus, besides the universal character of the alcohol family (the formation of ethers) has the property of forming aldehydic bodies (acetones) by the loss of two atoms of H, $\{CH(HO)\}''$ becoming $(CO)''$; and in that subgenus which contains the radical $\{CH_2(HO)\}'$ (or in which one of the R's is H), this aldehydic body is a true aldehyde, capable of forming an acid by further oxidation. When none of the equivalents of the carbon atom in the generic radical are directly saturated with H, the alcohol is incapable of producing an aldehyde or acetone; and, in this case, we have the characteristic radical reduced to $\{C(HO)\}'''$, as in Butlerow's trimethyl alcohol. We thus see that the most general form of alcohol is $C(HO)R_3$ (where R_3 represents one triatomic, or one diatomic and one monatomic, or three monatomic radicals); and the genera, sub-genera, and individuals of this family are determined by the nature of the radical or radicals, combined with the family radical $\{C(HO)\}'''$. For convenience let us, in the meantime, represent this radical by the symbol Φ'''. The different subdivisions of the family will then be $R'''\Phi$, $R''R'\Phi$, and $R'_3\Phi$. If

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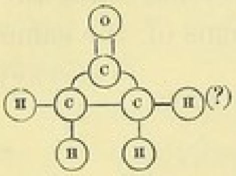
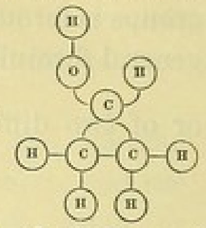
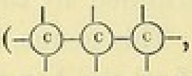
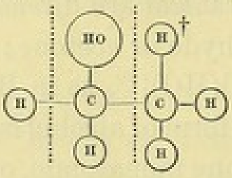
[*] I had proposed to express the radical $(COHO)'$ by the symbol Ξ, before I was aware that Butlerow had already used the symbol A to represent the same radical. While fully acknowledging the priority of Butlerow's recognition of this radical, I prefer to retain the symbol Ξ. By using such of the Greek capitals as differ from the Roman in form, to represent generic radicals, we avoid the danger of confounding them with elementary atoms.

the original and ingenious speculations of Kekulé on the constitution of the aromatic bodies should be experimentally confirmed, phenylic alcohol would be an example of the first form $(C_5H_5)'''\Phi$.* The second and third form may be subdivided into genera, having the generic radicals $(R'\Phi)''$. As we have seen, by far the most important of these is that containing $H\Phi$, and it may be convenient to express this by a separate symbol, say Θ''. Under this genus we have two forms, $R''\Theta$ and $R'_2\Theta$. The so-called ketones of the dibasic carbon acids (dicarbonsäuren) may be regarded as the aldehydes of unknown alcohols of the first form ; thus succinone



may be considered as the aldehyde of the unknown alcohol, ...



To the second form $R'_2\Theta$, belong the greater number of known alcohols, and a considerable number of bodies possessing alcoholic properties, though not generally classified with the alcohols. They form aldehydes or acetones by oxidation ; and this reaction is not confined to those substances to which the name alcohol is commonly applied : for instance, mesoxalic acid is the aldehyde (or acetone) of tartronic acid, alloxan that of dialuric acid, glyoxylic acid that of glycollic acid. Confining our attention to those substances of the form $R'_2\Theta$, in which R is of the form $(C_nH_{2n+1})'$, and has its C atoms arranged in the simplest way ( &c.), we may form the following series of sub-generic radicals $H\Theta$, $CH_3\Theta$, $C_2H_5\Theta$, &c. The first of these we have seen to be the radical of the "true" alcohols, and it seems probable that the second is that of the hydrates of the olefines. The arguments in favour of this view (which undoubtedly requires and admits of further experimental research) may be stated thus :—The first member of the series, the hydrate of ethylene, is identical with common alcohol, and has the formula † or, $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}\Theta$. The

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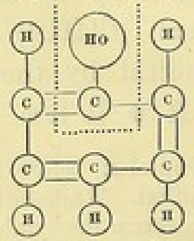
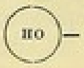
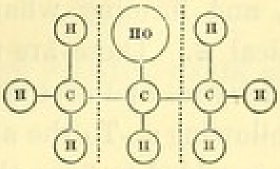
* Translating Kekulé's graphic formula for phenylic alcohol into the system used in this paper, we have



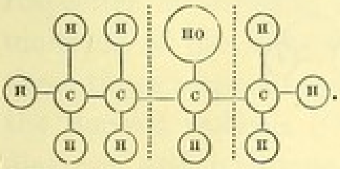
in which we have the triatomic radical C(HO) united to the triatomic radical C_5H_5.

† Using the symbol  as a contraction for .

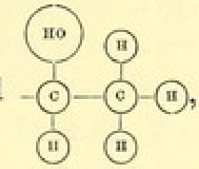
hydrate of propylene is almost certainly identical with the alcohol derived from acetone, which is



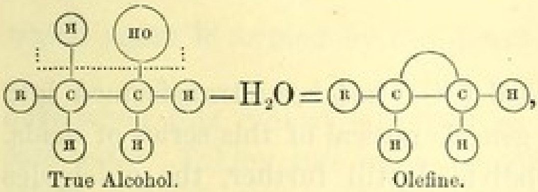
or $\left.\begin{array}{l}CH_3\\CH_3\end{array}\right\}\ominus$. The constitution of hydrate of butylene has not been directly ascertained, but as it is obviously *meta*meric with butylic alcohol, and as it is in the highest degree improbable that its C atoms are arranged in a different way, we may safely assume that its formula is $\left.\begin{array}{l}CH_3\\C_2H_5\end{array}\right\}\ominus$,



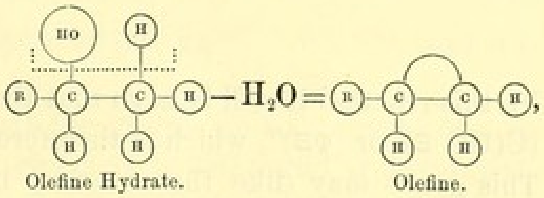
. In all these bodies we have the radical



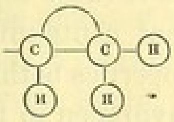
, $\left.\begin{array}{l}CH_3\\ \cdot\end{array}\right\}\ominus$, and from the similarity of the method by which the others are produced, it is reasonable to infer that they are similarly constituted. If so, while the "true" alcohols have the water residue united to what we may call a *terminal* C atom, the olefine hydrates have the water residue united, not to this, but to the C atom next to it. As both alcohols give the olefine by dehydration, the carbon equivalents deprived of HO and H, must be those which are combined with HO, the one in the one, and the other in the other. Thus:—



and

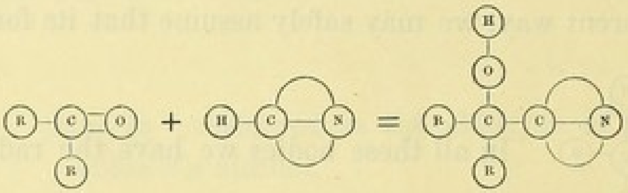


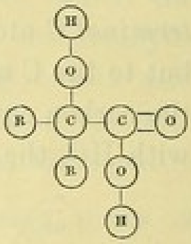
So that

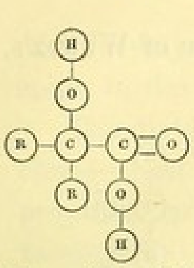
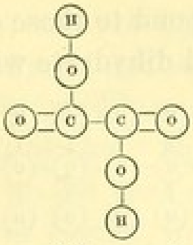


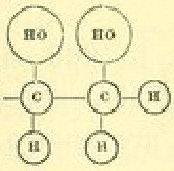
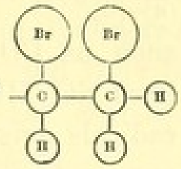
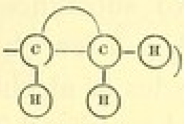
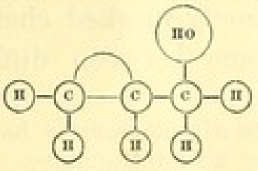
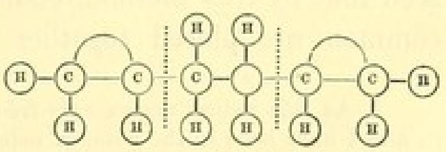
$(C_2H_3)'$ must be the generic radical of the olefines. As the true alcohols are formed from the aldehydes, or, as they may be called, the formo-ketones (as produced by distilling a mixture of formiate of lime with another lime salt), so we may presume that the alcohols $\left.\begin{array}{l}CH_3\\R\end{array}\right\}\ominus$, may be produced from the aceto-ketones (the ketones formed by distilling acetate of lime with other lime salts), and the same is no doubt the case with all the other genera of pseudo-alcohols of the form $R'_2\ominus$. $(HCO)'$, $(CH_3CO)'$, $(C_2H_5CO)'$, &c., becoming $(H\ominus')$, $(CH_3\ominus)'$, $(C_2H_5\ominus)'$, &c. The same considerations would, of course, apply to other series besides that of completely saturated bodies, but it is unnecessary to do more than mention this as Linnemann's benzhydrol $(C_6H_5)_2\ominus$ stands, as yet, alone as a pseudo-alcohol of this class among non-saturated bodies.

Derived from the aldehydes and acetones, we have another series of substances, having well-marked reactions in common, and forming what we may call a subgenus of the genus containing the radical Ξ. These are the acids obtained by the action of HCl and HCN, on the aldehydes and acetones. The mode of formation of these acids appears to be the following:—To the aldehyde or ketone HCN is first added in the same way as H_2 is added to form the alcohol, a body which may be called an *oxynitrile* being then produced.

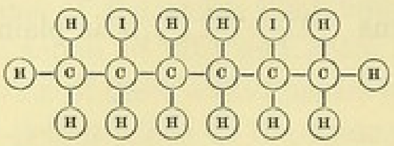


(this stage of the reaction can be traced in the case of bitter almond-oil; the so-called hydrocyanate of bitter almond-oil being, no doubt, the nitrile of mandelic acid). In the second stage of the reaction this nitrile is decomposed (like other nitriles) by the HCl and water, yielding NH_4Cl, and the acid  by this reaction it will be seen that the radical $(CO)''$ has been transformed into $(C(HO)\Xi)''$ or $(\Phi\Xi)''$, which is therefore the generic radical of this series of acids. This genus may (like the acetones) be subdivided still further, the aldehydes giving rise to acids containing $(\Phi H\Xi)'$ (or $\Theta\Xi$), the acetoketones to those containing $(\Phi CH_3\Xi)'$, &c. The best known of these subdivisions is that containing $(\Theta\Xi)'$. As indicated by the generic radical, these bodies have the properties both of acids and alcohols, giving rise to salts by the replacement of the hydrogen in the Ξ by metals, and to ethers by the replacement of the (HO) in the Θ by salt radicals (acids minus H). Some of them, at least, seem capable of forming aldehydes; for, as **Debus** has pointed out, glyoxylic acid is the aldehyde of glycollic acid. (It is worthy of note, that glycollic acid is the only member of the series which is a "true" alcohol, containing the radical $(H\Theta)'$, and giving rise, by oxidation, to an aldehyde and an acid—glyoxylic and oxalic acids). The typical formulæ of **Frankland** and **Duppa** indicate in a different way the same constitution as that expressed by the radical formulæ above; $C_2\left\{\begin{matrix}O''\\HO\\HO\\R_2\end{matrix}\right.$ being obviously identical with

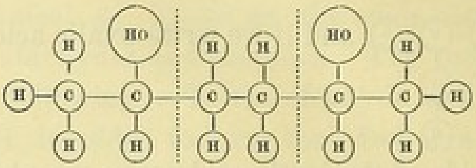
 and if we write oxalic acid $(\Xi)_2$, thus  it is plain that the acids of the lactic acid series may be derived from it by replacing O'' by R_2.

Kolbe long ago suggested, and Maxwell Simpson has since proved, that the dibasic and tribasic carbon acids are related to two and three molecules respective of carbonic acid, in the same way as the monobasic acids are to one molecule of the same substance. They therefore contain the radical Ξ two and three times respectively. Similarly, we might expect to find bodies containing the derived radicals (COH), (CH_2HO), &c., two or three times, forming thus diatomic and triatomic aldehydes, alcohols, &c. We only know one diatomic aldehyde, glyoxal $(COH)_2$, and with certainty, only one diatomic *true* alcohol, glycol $(CH_2HO)_2$. From the way in which the other glycols are formed, it will be seen, that if the view of the structure of the olefines suggested above be correct, they contain the radical  (formed by replacing Br by HO in  which again is formed by the direct addition of Br_2, to ), and it is only when this radical is united to H that the glycol can be a *true* alcohol *on both sides*. Taking this view, propylenic glycol is a compound of the radicals $(H\Theta)'$, and $(CH_3\Theta)'$; amylenic glycol of $(H\Theta)'$ and $(C_3H_7\Theta)'$, and so of the others, one of the atoms of water residue being in the position of the HO in a true alcohol, the other in that of an olefine-hydrate. Of course, it is quite conceivable, and indeed very likely, that there are bodies which contain the radical (CH_2HO) twice or oftner, and are thus polyatomic *true* alcohols; but, with the exception of ethylenic glycol, they are as yet unknown. In treating of diatomic alcohols, we cannot pass over the curious body obtained by Wurtz, by the addition of water to allyl. A consideration of the chemical relations of acrylic acid, acrolein and allylic alcohol to propionic acid, propionic aldehyde and propylic alcohol indicates for allylic alcohol the formula  and for allyl 

It is therefore a diatomic olefine, containing the radical $(C_2H_3)'$ twice, and if its reactions correspond to those of the monatomic olefines the formulæ of WURTZ's, dihydriodate and dihydrate will be,—

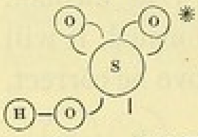


and



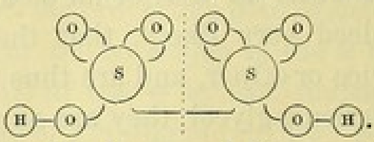
the latter will thus contain the radical $(CH_3\ominus)'$ twice, and be a diatomic olefine-hydrate.

The organic acids derived from sulphuric acid, and which are formed by the addition of SO_3 to organic substances containing hydrogen, stand in the same relation to sulphuric acid as the carbon acids (carbonsäuren) do to carbonic acid; in these we have an organic radical replacing one HO in $SO_2(HO)_2$. They therefore contain the radical $SO_2(HO)$; which, assuming the hexatomic character of the sulphur atom in sulphuric acid, may be represented by the graphic formula,



* As we have numerous generic radicals derived from $\{(CO)\ HO\}'$ such as COH, $CH_2(HO)$, we might expect to find similar derived radicals from $SO_2(HO)$, and there can be little doubt that substances containing such radicals exist; but as yet very few of them are known. Thus we have only one or two substances corresponding to the acetones, such as sulpho-benzid, $(C_6H_5)_2SO_2$; a few chlorides containing SO_2Cl, but no bodies corresponding to the aldehydes or alcohols.† The remarkable substance discovered by V. OEFELE, and named by him "Triæthyl sulphin oxydhydrat," and which has the formula $S^{iv}(C_2H_5)_3(HO)$, is a proof of the possibility of such bodies. This substance has the same relation to sulphurous acid that BUTLEROW's trimethyl alcohol has to carbonic acid.

As the radical COHO unites with itself to form oxalic acid, so we have SO_2HO, forming hyposulphuric acid $(SO_2HO)_2$



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The examples of generic radicals might be considerably increased in number, but as the purpose of this paper is not so much to tabulate known substances, as to show how this may be done, those given above may suffice. It will be seen that by this method, bodies having strongly marked chemical reactions in common are placed together. The relations between different genera are

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* As this radical occurs very frequently, it may be advantageous to have a single symbol for it, and I have been in the habit of using the Greek letter Σ for this purpose. Thus we have $CH_3\Xi$, acetic acid; $CH_3\Sigma$ methylsulphuric acid; $CH_2\Xi\Sigma$ sulphacetic acid, &c.

† See KOLBÉ, Lehrbuch der Organischen Chemie, Bd. ii. s. 742.

prominently brought forward, and the vacancies, not yet filled up by experiment, in the list of conceivable compounds, distinctly pointed out.

The division of molecules into two parts, one more readily undergoing chemical change than the other, presents certain analogies to the "Theory of Copulæ," proposed by BERZELIUS. This is most marked in the case of the acids containing $(COHO)'$ and $(SO_2HO)'$. On the theory of copulæ, these acids contain oxalic acid C_2O_3, H_2O, or hyposulphuric acid S_2O_5, H_2O, and a copula. Thus acetic acid was considered as C_2H_6, C_2O_3, H_2O, sulpho-benzolic acid as $C_{12}H_{10}$, S_2O_5, H_2O, &c.; according to the view which is taken in this paper, acetic acid contains the *half* of C_2H_6 (methyl), and the *half* of oxalic acid; sulpho-benzolic acid, the *half* of $C_{12}H_{10}$ (phenyl), and the *half* of hyposulphuric acid. In the same way, the older chemists regarded hydrochloric acid as H_2Cl_2, a compound of the *molecule* H_2, with the *molecule* Cl_2, while we now consider it as containing the *halves* of these molecules. It is therefore as correct to say, that acetic acid is a compound of methyl and oxalic acid, as that hydrochloric acid is a compound of hydrogen and chlorine. To prevent confusion, it is however better, whenever it can be done, to have separate names for the *radical* and the *substance*. Thus we may call $(COHO)'$ *Carboxyl* (as proposed by BAYER), and distinguish it from $(COHO)_2$ oxalic acid, $(SO_2HO)'$ might be called *Sulphoxyl*, and thus be distinguished from $(SO_2HO)_2$ hyposulphuric acid. Even in the case of those radicals whose names are the same as the isomeric substances, we may, in some instances, make the distinction; thus $(CH_3)'$ is methyl, $(CH_3)_2$ methyl gas, $(CN)'$ cyanogen, $(CN)_2$ cyanogen gas, Cl' chlorine, Cl_2 chlorine gas.

In conclusion, it may be interesting to enumerate some of those substances which consist *entirely* of generic radicals—all of whose reactions are therefore generic reactions—thus we have cyanogen gas $(CN)_2$, consisting of two atoms of the generic radical of the nitriles united together; glyoxal $(COH)_2$; glycol $(CH_2HO)_2$, or $(\Theta H)_2$; oxalic acid $(COHO)_2$, or Ξ_2; hyposulphuric acid $(SO_2HO)_2$, or Σ_2,; tartaric acid (probably) $(CH(HO))_2\,(COHO)_2$, or $(\Theta\Xi)_2$; glycolic acid $(CH_2HO)\,(COHO)$, or $(\Theta H)\Xi$; glyoxylic acid $(COH)\,(COHO)$, or $(COH)\Xi$; tartronic acid $CH(HO)\,(COHO)_2$, or $\Theta\Xi_2$; glycerine (probably) $(CH_2HO)_2(CH(HO))$, or $\Theta\,(\Theta H)_2$; glyceric acid $(CH_2HO)\,(CH(HO))\,(COHO)$, or $(\Theta H)\,(\Xi\Theta)$; mesoxalic acid $(CO)\,(COHO)_2$, or $CO\Xi_2$.

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