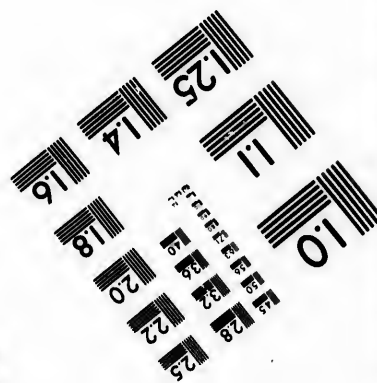
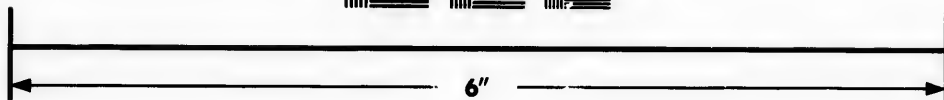


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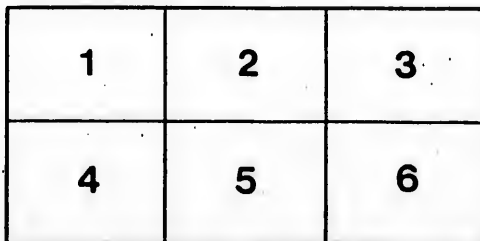
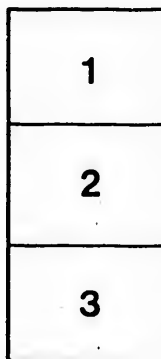
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MARCH 1854.

ON THE THEORETICAL RELATIONS OF WATER
AND HYDROGEN; by T. STERRY-HUNT, Chemist to the
Geological Commission of Canada.

In carrying out his theory of types, M. Laurent proposed to consider water H_2O_2 , having its equivalent represented by four volumes of vapor, as the type of the oxyds like MaO_2 , of the hydroxyds $(MH)O_2$, and of the sulphurets corresponding to these two classes. By his system of compound radicals, Liebig had extended to organic chemistry the nomenclature of Lavoisier, and he looked upon spirit of wine $C_2H_5O_2$, as the hydrated oxyd of a radical ethyl ($C_2H_5 = Et$), while hydric ether C_2H_5O , was the simple oxyd of the same radical. But as ether-vapor contains in the same volume, twice as much carbon as the vapor of alcohol, Gerhardt had already proposed to double the formula of ether, and Laurent now showed that while alcohol is to be regarded as the hydroxyd of ethyl $(EtH)O_2$, or water in which ethyl replaces an equivalent of hydrogen, ether is the anhydrous oxyd, in which the second equivalent of hydrogen is replaced, and should be written Et_2O_2 . Hence while ether is neutral, alcohol is monobasic, having an equivalent of hydrogen.



replaceable by a metal, and is the type of monobasic vinic acids, while water is the type of bibasic acids. (*Laurent, Recherches sur les Combinaisons azotées. Ann. de Chim. et de Phys., Nov. 1836.*)

In a review of that remarkable essay, published in this Journal for Sept., 1848 (vol. vi, p. 173), I suggested that this view was "susceptible of still farther extension, and that we may include in the same type all those saline combinations (acids) *which contain oxygen.*" I referred to the hypochlorites ClO , MO , as derivatives of the type H_2O_2 , in which Cl replaces H , being $(\text{ClH})\text{O}_2$, and $(\text{ClM})\text{O}_2$, while anhydrous hypochlorous acid is Cl_2O_2 , the result of a complete substitution. "In the same manner nitric acid, NHO_2 , is a monobasic salt (i. e. acid), corresponding to water in which NO_2 is substituted for H , as in many organic compounds; we have then $(\text{NO}_2, \text{H})\text{O}$ and $(\text{NO}_2, \text{M})\text{O}$;" or $(\text{NO}_2, \text{H})\text{O}_2$ in the notation adopted above. "As an adaptation of this idea to bibasic compounds, sulphuric acid, SH_2O_4 , is to be regarded as water in which SHO_2 replaces H ; thus $(\text{SHO}_2, \text{H})\text{O}$. As the replacing elements contain an equivalent of hydrogen which is saline (i. e. replaceable by a metal), the acid is bibasic. When the hydrogen in SHO_2 is replaced by a metal, we have a class of acid sulphates like $(\text{SKO}_2, \text{H})\text{O}$. The complete replacement of hydrogen in the original type yields $(\text{SHO}_2)_2\text{O}$, which is the Nordhausen acid commonly represented by $2\text{SO}_3, \text{H}_2\text{O}$. This latter compound as Gerhardt has shown, corresponds to the anhydrous bisulphate of potash."

"The tribasic acids may equally be reduced to the same type, if we conceive the elements which replace one equivalent of hydrogen, to be bibasic instead of neutral or monobasic; phosphoric acid, PH_3O_4 is $(\text{PH}_2\text{O}_2, \text{H})\text{O}$."

"The primitive saline type is then essentially bibasic, and is presented in its most elemental form in water, while the simplest type of the monobasic salt, which is a derivative of

the last, is found in hypochlorous acid." p. 174. This view of the derivation of polybasic acids is illustrated by the bibasic sulphacetic, and the tribasic sulphosuccinic acid.

On page 177 we further remark, that "the binary molecule of the metals, hydrogen, chlorine, bromine, etc. will be seen to be the type of an immense number of combinations, embracing the various alloys and amalgams, the hydracids like hydrochloric acid, with their corresponding salts, and such compounds as ClBr and ClI , while ICl_3 is referable to a triple molecule of these elements, represented by H_6 ; to this type belong the perchlorids of antimony, arsenic and phosphorus, while the corresponding trichlorids form a double molecule."

In a subsequent Essay on Chemical Classification read before the American Association for the Advancement of Science, at Philadelphia, in September, 1848, and published in this Journal for May and July, 1849, (vols. vii and viii,) we observed that the relation between alcohol and acetene is that which subsists between the two types H_2O_2 , and H_2 , acetene being hydrogen in which ethyle replaces H, thus C_2H_2 , $\text{H}=\text{C}_2\text{H}_2$, while hydrochloric ether is a chlorinized hydrocarbon corresponding to hydrochloric acid, so that having repeated what has been already cited as to the type H_2 , we add, "moreover it follows from the relations of HCl to the chlorinized hydrocarbons, that it (H_2) is the type of all the hydrocarbons, as well as of the alkaloids, which may be described as amidized species of them, and are equally susceptible of substitutions by chlorine." It was also remarked that "as many neutral oxygenized compounds, which do not possess the saline character, are still derivatives of acids which are referable to the type H_2O_2 , we may regard all oxygenized bodies as belonging to this type." "While nitric acid is NHO_3 , or $(\text{NO}_2, \text{H})_2\text{O}$, the result of the complete replacement of H by NO_2 will be $(\text{NO}_2)_2\text{O}$, or the unknown dry nitric acid, homologue of the so-called anhy-

drous phosphoric and arsenic acids, which are equally ($\text{PO}_2)_2\text{O}$, etc." (Vol. viii, p. 92).

One of the objects proposed in the essay just quoted, was a comparison of the views of Gerhardt and Liebig with regard to the formation of ethers, amids, and allied bodies. Gerhardt in accordance with the electro-chemical theory of Berzelius, had considered the acids in these reactions to be electro-negative by their oxygen, while the alcohols, ammonia, and the hydrocarbons were electro-positive by their hydrogen, so that these bodies *minus* H_2 , replaced O_2 in the acid. To this view we objected that it leaves unexplained that change in the basic relations of the acid, which Liebig rightly understood when he compared the ethers to salts, and represented the acid as losing H , which is replaced by the elements of the alcohol *minus* HO_2 . This theory, unlike that of Gerhardt, made the ethers of the hydracids enter into the same class with those of the oxacids; at the same time it did not include those bodies which are produced with the elimination of H_2O_2 , by the action of oxygen acids upon ammonia and hydrocarbons, and which were recognized in Gerhardt's system, as completely analogous to the ethers in the mode of their formation. Here the compound radical theory is found to be defective, although the analogy which forms its point of departure is correct. In concluding this comparison we remarked that "we are led to recognize the view of Liebig, *apart from his ideas of dualism, and his theory of compound radicals*, as the one fundamentally true." (Vol. vii, p. 405.)

In this Journal for March, 1848, (vol. v, p. 263,) we observed that the relation of wood-spirit to acetonitryl is the same as that of water to hydrocyanic acid, and that water differs from wood-spirit, precisely as this last differs from spirit of wine, so that the relation of homology, recognized by Gerhardt in the compounds of carbon, is extended to water and hydrogen; for from the relations which we

have asserted between H_2O_2 , and H_2 , it follows that while water is the homologue of the alcohols, hydrogen H_2 is the homologue of acetene C_2H_2 , (Et H,) and of formene C_3H_4 , (Me H) which Frankland calls hydrids of ethyl and methyl, as well as of his zinco-methyl C_2H_3 , Zn. The bodies which he regards as the alcohol radicals are still homologues of hydrogen, the result of a complete substitution, and are $(C_2H_5)_2$ etc., like benzile $C_{12}H_{12}O_4$, which is Bz_2 , while bitter-almond oil is BzH .

In the Journal for January, 1850 (vol. ix, p. 65), this is again referred to, and we remark that as water is to be regarded as the homologue of the alcohols, it follows from the principles already laid down "that the ethers are homologous with their parent acids," a point which was illustrated by the action of the cyanic ethers with ammonia; while the volatile bases of Wurtz "sustain to their corresponding alcohols, the same relation that ammonia does to water." In volume xiii, p. 206, we repeat, "water is not only the analogue, but the strict homologue of the alcohols, so that the molecule H_2 is the equivalent (homologue) of C_2H_6 , and its homologues, and H of ethyl and methyl; (the hypothetical radicals.)"

The question whether these homologues of hydrogen H_2 are to be regarded as the radicals of the alcohols and ethers, has been discussed by Gerhardt, Hofmann, and others, but resolves itself into this; Frankland's ethyl is to EtCl what Zn_2 is to ZnCl, and H_2 to HCl; the metals, hydrogen and chlorine always present a dualism in their reactions, as marked as ethyl, kakodyl and cyanogen.

Williamson (*Philos. Mag.*, Nov., 1850) has made a beautiful application of Laurent's theory of the alcohols; by the action of potassic alcohol (Et K) O_2 upon hydriodic ether, Et I, he obtained KI, and Et $_2O_2$, and by a similar process mixed ethers, such as (Et Me) O_2 . He at the same time explained the theory of the ordinary ether process, as the reaction

between sulphovinic acid, $S_2(Et\ H)O_2$, and $(Et\ H)O_2$, giving $S_2H_2O_2$, and Et_2O_2 . Meanwhile Chancel, following out the same idea, announced almost simultaneously with Williamson, the production of hydric ether by the distillation of sulphovinate of potash with potassic alcohol; by the reaction of oxalovinate with sulphomethylate of potash, he also obtained a mixed oxalic ether $C_4(Et\ Me)O_2$, oxalic acid being $C_4H_2O_6$.

Still more recently Gerhardt has announced the production of a class of bodies, which he describes as the anhydrids of the monobasic organic acids. He had formerly regarded the production of anhydrids as characteristic of polybasic acids, because he would not admit the theoretical derivation of monobasic acids from a bibasic type H_2O_2 , the complete replacement of whose hydrogen should, as I have long ago shown, yield neutral anhydrids (like the anhydrous nitric acid since discovered), sustaining to the corresponding acids the relation of hydric ether to alcohol. According to the view which I advanced in 1848, acetic acid, $C_4H_4O_4$, was represented by $(C_4H_3O_2, H)O_2$, and the anhydrid would be $(C_4H_3O_2)_2O_2 = C_8H_6O_6$, corresponding to four volumes of vapor. This body has been obtained by Gerhardt as well as the butyric, valeric, benzoic, and cinnamic anhydrids, besides mixed species analogous to the mixed ethers, such as the aceto-benzoic anhydrid, which contains the elements of one equivalent each of acetic and benzoic acids, *minus* H_2O_2 . These bodies are of course neutral, and regenerate acids by assimilating the elements of water.

The process by which these bodies are obtained, is very instructive : when the perchlorid of phosphorus PCl_5 , or the oxychlorid PO_2Cl_3 acts upon a salt like the acetate of potash, a body represented by $C_4H_3Cl\ O_2$ is obtained, which bears the same relation to acetic acid that hydrochloric ether does to alcohol; by the action of this acetic chlorid upon acetate of potash, chlorid of potassium and anhydrous acetic acid are

produced. Alcohol $C_4H_6O_2$ being represented as $(Et\ H)O_2$, we may write the formula of acetic acid $(Ac\ H)O_2$, $(C_4H_5O_2=Ac)$, while the chlorid is $Ac\ Cl$. This corresponds to hydrochloric or hydriodic ether, while acetate of potash $(Ac\ K)O_2$, is analogous to potassic alcohol. The process is then similar to that by which Williamson obtained hydric ether: $Ac\ Cl + (Ac\ K)O_2 = K\ Cl + Ac_2O_2$, or the anhydrous acid.

The reaction in all these cases is, as I have pointed out in the paper before quoted (vol. viii, p. 93) identical in essence with that between $H\ Cl$ and $(K\ H)O_2$, yielding an alkaline chlorid $K\ Cl$, and water H_2O_2 , the prototype of all the above acids, ethers, alcohols, and anhydrids. We have there also remarked that H_2O_2 is to be regarded as a derivative of hydrogen, H_2 , and that it is often difficult to distinguish between the types. Thus, for example, the acetic chlorid might be regarded as a chlorinized aldehyde $(C_4H_5, Cl)O_2$, belonging to the second type, while its reactions permit us to compare it with the hydrochloric ethers of the type H_2 . It must be kept in mind that although the apparent dualism deduced from the results of chemical change, is subject to but very simple variations in the elements, it is exhibited in so many different ways in the higher species, that we cannot assign an absolute value to any hypotheses based upon their changes.

I have been particular in again bringing forward these views, because they now belong to the history of chemical theory, and because after having maintained them alone since 1848, and having insisted upon them in various ways in my communications to this Journal, I now find them brought forward by Williamson, Brodie and Gerhardt. This latter chemist in a paper presented to the French Academy in June 1852, and published in the *Annales de Chimie et de Physique* for March, 1853, abandons those theories to which I long since objected, and brings forward, with a similarity of thought and expression not to be mistaken, the views upon

which I have here insisted. (See us above pp. 336—342.

Williamson in a paper read before the British Association in July, in 1851, has expressed the same ideas with regard to the typical relations of water, and is recognized by the English editor of Gmelin's Handbook (vol. vii, pp. 17 and 201) as the author of the theory. See also Brodie's lecture before the Royal Institution in May, 1853 (Chemical Gazette, Aug., 1st) "On the formation of hydrogen and its homologues."

It is gratifying to find that the views which I have so long maintained, are at last recognized by chemists, and are found productive of beautiful and important results; but it would be only just in these chemists, to have admitted the priority, by three or four years, of my own published views, anticipating the brilliant series of discoveries which have served them as the basis of their generalizations.

Montréal, dec. 20, 1853.

