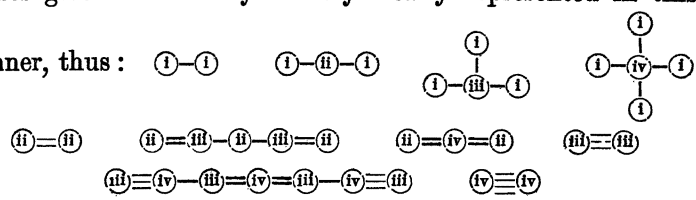
Art. XLII.—*On normal and derived Acids;* by George F. Barker.*

The law of saturation by equivalence, introduced into chemistry by Kekulé, determines at once the formula of every possible binary compound.† Assuming that the simple radicals may be divided into four groups, it will be seen that the number of binary compounds is limited to the following ten classes; monads with monads, as $K'Cl'$; with dyads, as $O''H'_2$; with triads, as $Au'''Cl'_3$; and with tetrads, as $Pt^{iv}I'_4$; dyads with dyads, as $Mg''O''$; with triads, as $As'''_2O''_3$; and with tetrads, as $C^{iv}O''_2$; triads, with triads, as $B'''N'''$; and with tetrads, as $Zr^{iv}{}_3N'''_4$; and finally tetrads with tetrads, as $Pt^{iv}Si^{iv}$. The number of atoms therefore, which enter into such compounds, is determined by a very simple mathematical law. On this fact rests the possibility of graphic representation. Of the various methods in use, that of A. Crum Brown, in which the atom is represented by a circle, and its equivalence by projecting lines called bonds or units of attraction, is perhaps the best. As every compound body must be saturated, i. e., have all its bonds engaged, the ten classes given above may be very clearly represented in this manner, thus:



Here it will be noticed, no bonds are exchanged by similar atoms; i. e., those of the same element.

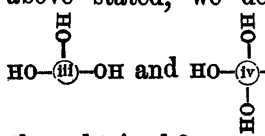
* In this paper, H=1, O=16, S=32, **C**=24, **Al**=55, **Si**=56, etc.

† When two radicals unite together, the number of atoms of each required for mutual saturation, is obtained by dividing the least common multiple of the numbers representing their equivalencies by the equivalence of each. Generally, the number of atoms of each radical is inversely as its equivalence, four triad atoms saturating three tetrads, for example. Atoms thus combined, alternate with each other, the two units of attraction in each exchange, belonging to dissimilar radicals.

When, however, similar atoms unite directly, two units of attraction disappear for each pair of atoms, being occupied in holding these atoms together. Two tetrad atoms thus combined, have therefore an equivalence of six, three such atoms of eight, four of ten, etc. Or, as Kekulé has shown (Lehrbuch, 1861, i, 163), the number of units of attraction left free by the union of any number of carbon atoms is equal to twice the number of such atoms, plus two (=2n+2). C. G. Foster has extended this law to all the poly-equivalent radicals (Watts' Dictionary, i, 1007) giving the formula E=S−2(n−1), in which E indicates the group-equivalence, *n* the number of poly-equivalent atoms, and S the sum of their units of attraction. By this formula, the highest number of hydrogen atoms which can be united with ten carbon atoms for example, is 40−2(10−1)=22, giving the hydrocarbon $C_{10}H_{22}$. From this a series of lower compounds may be formed, each differing from the next higher, by H_2.

If now any of these bonds be left unsatisfied, or in other words, if the chemical edifice represented by the molecule be incomplete, it is evident that the whole structure, whatever its complexity, is capable of entering into combination by its free bond or bonds. Hence in this case, the compound body will act precisely like a simple radical having the same equivalence. Such unsaturated bodies are called compound radicals and their equivalence or combining power is exactly equal to the number of unsatisfied bonds. These compound radicals, therefore, may be used in place of the simple radicals, in the formulas above given; thus forming a new set of compounds, which, since the number of compound radicals possible is almost unlimited, are exceedingly numerous. The compound radicals most in use are those derived from the hydrogen compounds of the different groups of simple radicals, by successive unsaturation. If from the ordinary so-called types, HCl, H_2O, H_3N, H_4C an atom of hydrogen be removed, there is left Cl′, (HO)′, $(H_2N)'$, $(H_3C)'$, all monad compound radicals. By continuing the process where it is possible, radicals of higher equivalence are thus produced.

With these facts premised, I pass to the subject of the present paper; i. e., the consideration of the bodies which result from the union of the monad compound radical hydryl (HO)′ with the simple radicals. Representing H_2O by Ⓗ–Ⓞ–Ⓗ, hydryl is Ⓗ–Ⓞ–, which may be represented either by a larger circle or by the letters alone, thus HO–. From the principles above stated, we deduce the formulas Ⓘ–OH HO–Ⓘ–OH



HO–Ⓘⓘⓘ–OH and HO–Ⓘⓥ–OH. What is the character of the bodies thus obtained?

A reply to this question becomes possible only by classifying the simple radicals according to their electro-chemical characters. In the method of classification given above, the elements are divided according to the *quantity* of their combining power i. e., to their equivalence; here the division is into positive and negative, according to the *quality* of this combining power. When a *positive* simple radical combines with hydryl, a *base* is produced; when a *negative* simple radical so unites, an *acid* results. If, for example, the vertical columns in the table below, represent the equivalence, increasing from left to right, and the horizontal the electro-chemical character, we may illustrate these statements as follows:—

	Monad.	*Dyad.*	*Triad.*	*Tetrad.*
−	Cl′(HO)	$S''(HO)_2$	$B'''(HO)_3$	$C^{iv}(HO)_4$
+	K′(HO)	$Ca''(HO)_2$	$Bi'''(HO)_3$	$Zr^{iv}(HO)_4$

The formulas in the upper row represent well known acids, and those in the lower, as well known bases.

It has been thus far assumed that the equivalence of a radical is invariable. But it seems evident that when one element combines with another in more than one proportion, its combining power must be different in the two cases. Thus in stannic oxyd SnO_2 and stannous oxyd SnO; tin is evidently a tetrad in the former case and a dyad in the latter. In all cases, however, the equivalence changes by two, either up or down; it therefore never alters from even to odd or the reverse. A dyad may act as a tetrad or hexad; a monad as a triad, pentad or heptad. Applying this principle now to the compounds of the radicals with hydryl, we notice that the negative radicals vary their equivalence by several stages, forming a series of acids; but that the positive radicals rarely form more than a single series of bases, their equivalence being fixed at a single stage. With negative radicals, we may have for example:—

Monad.	*Dyad.*	*Triad.*	*Tetrad.*
$Cl'(HO)$	$S''(HO)_2$	$P'''(HO)_3$	$Sn^{iv}(HO)_4$
$Cl'''(HO)_3$	$S^{iv}(HO)_4$	$P^{v}(HO)_5$	- - - - -
$Cl^{v}(HO)_5$	$S^{vi}(HO)_6$	- - - -	- - - - -
$Cl^{vii}(HO)_7$	- - - -	- - - -	- - - - -

But the only instance of such changes with the positive radicals, is in the case of the perhydrates of the alkaline earths; as $Ba^{iv}(HO)_4$, $Sr^{iv}(HO)_4$, etc., the composition of which, however, is not fully decided.

I. It will be noticed in the formulas of the acids above given that the number of atoms of oxygen and of hydrogen are equal, and also that they are equal to the equivalence of the radical. Such acids, thus simply derived, I propose to call normal acids. A normal acid then, is one which contains as many atoms of oxygen and of hydrogen as is equal to the equivalence of the radical. They may be designated by prefixing *ortho* to the name of the acid, as proposed by Odling. Fixing now the acid termination *ic* for each group of the negative elements, the other terminations are readily obtained by the ordinary rule. Thus in the chlorine group, the radical in the *ic* acid has an equivalence of five; in the sulphur group, of six; in the nitrogen group, of five; and in the carbon group, of four. The acids in the above tables have consequently the following names:—

$Cl'(HO)$ Ortho-hypochlorous acid, $S''(HO)_2$ Ortho-hyposulphurous acid.
$Cl'''(HO)_3$ Ortho-chlorous acid, $S^{iv}(HO)_4$ Ortho-sulphurous acid.
$Cl^{v}(HO)_5$ Ortho-chloric acid, $S^{vi}(HO)_6$ Ortho-sulphuric acid.
$Cl^{vii}(HO)_7$ Ortho-perchloric acid,

$P'''(HO)_3$ Ortho-phosphorous acid, $Sn^{iv}(HO)_4$ Ortho-stannic acid.
$P^{v}(HO)_5$ Ortho-phosphoric acid.

In all the ortho acids the number of atoms of replaceable hydrogen, and therefore the basicity, is equal to the equivalence of the radical. Quite a number of these acids are known, either in the free state or in their salts. Of these, ortho-hypochlorous HClO, and hypo-bromous HBrO, ortho-iodous H_3IO_3, ortho-hyposulphurous H_2SO_2, ortho-nitrous H_3NO_3, ortho-boric H_3BO_3, ortho-carbonic H_4CO_4, silicic H_4SiO_4, stannic H_4SnO_4, and titanic H_4TiO_4, and ortho-antimonic acids H_5SbO_5 may be mentioned.

II. But it is at once evident that this simplicity of constitution of the acids is far from universal; indeed the large majority of acids have a composition essentially different. In general, the acids of the chlorine group are monobasic, those of the sulphur group dibasic, those of the nitrogen group mono- or tribasic, and those of the carbon group dibasic. The basicity of an acid containing a single atom of a perissad radical, however, is never even, nor that containing an artiad radical odd.

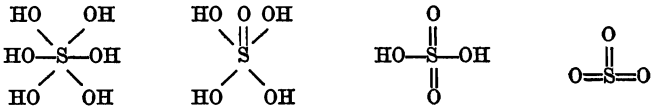
Now an acid, like any other ternary, may be formed by the union of two binaries; but in the case of acids, one of these binaries is water. Thus Cl_2O hypochlorous oxyd uniting with hydric oxyd H_2O gives $H_2Cl_2O_2$ or $(HClO)_2$, two molecules of ortho-hypochlorous acid. So SO_3 sulphuric oxyd, and H_2O form H_2SO_4, the ordinary sulphuric acid. Conversely, abstraction of the elements of water from an acid yields again the negative oxyd or anhydrid. A false view of this fact it was, which gave rise to the old dualistic formulas, in which water is represented as existing as such in the acids. In all monobasic acids, however, two molecules of the acid are required to furnish one molecule of water; in dibasic acids, one molecule is required, in tribasic acids $\frac{2}{3}$ of a molecule, and in tetrabasic acids $\frac{1}{2}$ a molecule. The number of molecules of water which can be added to a negative oxyd to form an acid is determined by the equivalence of the simple radical which it contains. Thus in SO, sulphur is a dyad, and only a single molecule of water can be added to it, $SO+H_2O=H_2SO_2$, thus producing the normal acid. In SO_2, sulphur is a tetrad and two such additions are possible before reaching ortho-sulphurous acid, $SO_2+H_2O=H_2SO_3$, and $SO_2+(H_2O)_2=H_4SO_4$. In SO_3, sulphur is a hexad and three molecules of water may unite successively, $SO_3+H_2O=H_2SO_4$, $SO_3+(H_2O)_2=H_4SO_5$, and $SO_3+(H_2O)_3=H_6SO_6$, yielding finally the normal acid as before. The reverse process also is readily performed. Indeed, Graham long ago showed that a single molecule of tribasic phosphoric acid by the loss of H_2O, afforded a monobasic phosphoric acid. In the passage then, from the normal acids to the negative oxyds (or anhydrids), there may be as

many intermediate acids as successive abstractions of H_2O from the normal acids, will permit. Thus, chlorine may yield

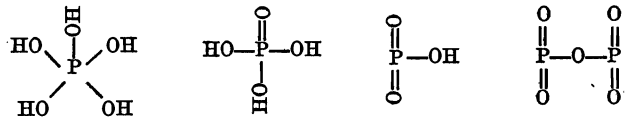
	Monad.	*Triad.*	*Pentad.*	*Heptad.*
Ortho,	$HClO$	H_3ClO_3	H_5ClO_5	H_7ClO_7.
Mono-meta,	....	$HClO_2$	H_3ClO_4	H_5ClO_6.
Di-meta,	....	....	$HClO_3$	H_3ClO_5.
Tri-meta,	....	....	....	$HClO_4$.

To the monobasic phosphoric acid which Graham obtained from the ordinary tribasic acid, by the removal of H_2O, he gave the name meta-phosphoric acid. And although the etymological signification of this prefix has entirely disappeared, yet it is so generally used in the science, that it may be well to retain it; and to define a meta-acid as one formed from an ortho-acid by the loss of one or more molecules of water. Moreover, since there may be several such acids, derived from a single ortho-acid, I propose to prefix the Greek numerals to the meta, in order to distinguish them; as in the above table, where ordinary chloric acid, being two removes from ortho-chloric acid, is named di-meta-chloric acid. Conversely by adding to the meta-acid the number of molecules of water indicated by the Greek numeral prefix, its corresponding ortho-acid is obtained.

From the foregoing considerations, the general conclusion may be drawn, that all acids are either ortho or meta-acids; the ortho-acids being formed by saturating all the free bonds of any negative radical by the monad hydryl; and the meta-acids being derived from these by the loss of the elements of water. It is plain then, that the equivalence of the radical is the same both in the normal acids and in those derived from them; and that they differ in the fact that in the former all the bonds are united to hydryl, while in the latter some of them are saturated by oxygen. This is very clearly represented by the graphic method. In the passage from ortho-sulphuric acid H_6SO_6 to the negative oxyd SO_3, we have



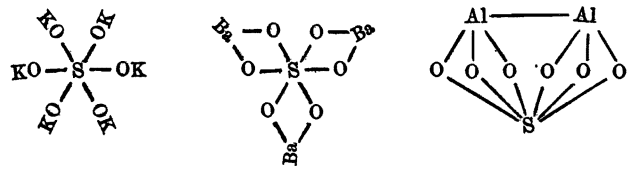
and in the case of phosphoric acid—



where finally, two molecules together losing H_2O, form phosphoric oxyd P_2O_5. It will be noticed that the tribasic acid, called by Odling ortho-phosphoric acid, is really mono-meta-phosphoric acid; while the common meta form is a di-meta-acid.

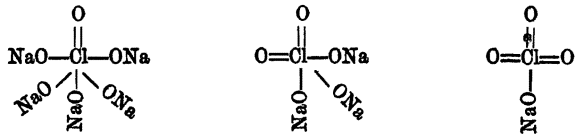
The above facts, we may remark in passing, throw much light on the manner of writing rational formulas. In all ternary compounds properly so called, the positive and the negative radicals are united by oxygen; indeed, this is the definition of an acid, a base and a salt. In all normal acids and their salts all the oxygen performs a linking function, thus:—

Potassic ortho-sulphate. Baric ortho-sulphate. Aluminic ortho-sulphate.



But in the derived or meta-acids a part of the oxygen is united with the radical by both its bonds, and hence takes no part in binding the radicals together.* In all the mono-meta acids one atom of oxygen is thus united, in the di-meta acids two, etc. For example,

Sodic mono-meta-perchlorate. Sodic di-meta-perchlorate. Sodic tri-meta-perchlorate.



This difference may be expressed by the ordinary formulas, thus: ortho salts Cl—OK, $\dot{S}=(OK)_2$, $B\equiv(OK)_3$ etc.; meta, $(PO)\equiv O_3Bi'''$, (NO_2)—OK, (ClO_3)—OAg, etc; or better in the form of the early typical formulas $\left.\begin{matrix}Cl'\\K\end{matrix}\right\}O$, $\left.\begin{matrix}S''\\Na_2\end{matrix}\right\}O_2$, $\left.\begin{matrix}B'''\\K_3\end{matrix}\right\}O_3$, and $\left.\begin{matrix}(PO)'''\\Bi'''\end{matrix}\right\}O_3$, $\left.\begin{matrix}(NO_2)'\\K\end{matrix}\right\}O$, $\left.\begin{matrix}(ClO_3)'\\Ag\end{matrix}\right\}O$. Hence it appears desirable that the form of the water type should be retained for rational formulas, since by it, this essential difference in the function of the oxygen may be readily indicated. $\left.\begin{matrix}(PO_2)'\\Cs\end{matrix}\right\}O$ designates at once cæsic di-meta-phosphate, $\left.\begin{matrix}(NO)'''\\Bi'''\end{matrix}\right\}O_3$ bismuthic mono-meta nitrate, $\left.\begin{matrix}(SO_2)''\\Mg''\end{matrix}\right\}O_2$ magnesic di-meta-sulphate, $\left.\begin{matrix}(SO)^{iv}\\Pt^{iv}\end{matrix}\right\}O_4$ platinic mono-meta-sulphate, $\left.\begin{matrix}(SO)''\\Na_2\end{matrix}\right\}O_2$

* This direct union is proved by the fact that this oxygen may be replaced by a radical of no uniting power, like the monad chlorine, for example, without breaking up the molecule; while the oxygen which unites the radicals to each other, cannot be so replaced without decomposing the molecule.

sodic mono-meta-sulphite, $\left.\begin{matrix}(ClO_3)'\\ Rb\end{matrix}\right\}O$, rubidic tri-meta-perchlorate, etc.

With the knowledge of the constitution of the acids above given, it may be interesting to examine the various groups of acid-forming or negative radicals, to see how far they conform to the law. Commencing with the monads, the chlorine group is the only one which forms acids. All the possible ortho and meta acids of chlorine are given in the table, page 388. Of these, those in italics, all of which are monobasic, are known with certainty, though polybasic acids of chlorine have been supposed, on experimental grounds, to exist.* In the case of iodine, however, mono-meta-iodic acid H_3IO_4, or $\left.\begin{matrix}(IO)'''\\ H_3\end{matrix}\right\}O_3$, and di-meta-iodic acid HIO_3 or $\left.\begin{matrix}(IO_2)'\\ H\end{matrix}\right\}O$ are known; so also are mono-meta-periodic acid H_5IO_6, di-meta-periodic acid H_3IO_5, and tri-meta-periodic acid HIO_4. Ortho-hypoiodous acid HIO, is supposed to exist. The acids of bromine have been but little studied; ortho-hypobromous acid $HBrO$, and di-meta-bromic acid $HBrO_3$ are the only ones satisfactorily established.

The dyad negative radicals include the sulphur and the iron groups. The substances composing the latter group, however, form bases when they act as dyads, are ambiguous as tetrads, and only form acids when they are hexads. Selenium and tellurium form no compounds which are not yielded by sulphur. The latter may stand, therefore, as the representative of both groups. It may form

	Dyad.	*Tetrad.*	*Hexad.*
Ortho-hyposulphurous	H_2SO_2.	sulphurous H_4SO_4.	sulphuric H_6SO_6
Mono-meta	.....	H_2SO_3	H_4SO_5
Di-meta	.....	.....	H_2SO_4

The three dibasic acids above given are the ordinary ones. But the two hydrates of sulphuric acid, so called, correspond to H_6SO_6 and H_4SO_5; and from these are obtained similar salts, as Hg''_3SO_6, and Zn''_3SO_5. The acids formed by the iron group are similar to those of hexad sulphur, the di-meta form being the more common; as in H_2CrO_4, H_2MnO_4, and H_2FeO_4. Chromium, however, forms acids, whose salts are well known, corresponding to the three sulphuric acids above given. With mercury and bismuth, there are the ortho-chromates Hg''_3CrO_6 and Bi'''_2CrO_6; and with lead, the mono-meta-chromate Pb''_2CrO_5. Manganese in its tetrad stage, appears capable of forming a mono-meta acid, corresponding to

* Crystallized hydric perchlorate, according to Roscoe, is H_3ClO_5 the di-meta form.

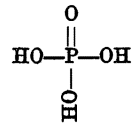
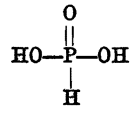
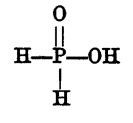
H_2SO^3. No true permanganic acid is known; since the acid so-called does not contain the metal as an octad. If its formula be written $HMnO_4$, monobasic, as the isomorphism of its salts with the perchlorates would seem to require, then manganese must be a heptad like chlorine; nor do we escape from this conclusion by writing it $H_2Mn_2O_8$, as will be seen farther on.

The acids of triad radicals may be divided into two groups; those of boron and gold, which have no higher equivalence: and those of nitrogen, phosphorus, arsenic, antimony, and bismuth, which have a quinquivalent stage. Of the former, boron forms an ortho-acid H_3BO_3 and a mono-meta-acid HBO_2; gold only a mono-meta-auric acid, $HAuO_2$. The acids of the nitrogen group may be represented as follows:

	Triad.		*Pentad.*
Ortho-nitrous	H_3NO_3	nitric	H_5NO_5
Mono-meta	$H\,NO_2$		H_3NO_4
Di-meta	.....		$H\,NO_3$

Salts have been obtained corresponding to all these acids of nitrogen; as plumbic ortho-nitrite $Pb''_3(NO_3)_2$, and potassic mono-meta nitrite KNO_2; dihydro-bismuthic ortho-nitrate $H_2Bi'''NO_5$, magnesic mono-meta-nitrate $Mg''_3(NO_4)_2$ and sodic di-meta-nitrate $NaNO_3$. No acid of triad phosphorus is known, if we except the calcic ortho-phosphite $Ca''_3(PO_3)_2$, corresponding to it. As quinquivalent however, all the above acids of phosphorus are known; the mineral libethenite is hydro-di-cupric ortho-phosphate HCu''_2PO_5; and triple phosphate dried at 100° C., has the formula $H_2(NH_4)MgPO_5$, di-hydro-ammonio-magnesic ortho-phosphate. Similar salts of iron and manganese have been obtained. The mono-meta-phosphoric acid H_3PO_4 is the ordinary tribasic form (Odling's ortho-acid), and the di-meta acid is the common monobasic or meta acid of Graham. It may here be remarked that the acids, called hypophosphorous and phosphorous, are misnamed, since the radical phosphorus is not trivalent in the latter and univalent in the former as analogy with the other acids, and indeed as the principles of nomenclature would require; but as Frankland has represented, both these acids contain phosphorus as a pentad. If the principles above stated be correct, it is evident that the number of atoms of basic hydrogen can never exceed those of the oxygen by which it is linked to the acid radical. In H_3PO_2 the hydrogen is in excess, and it is at once apparent that the acid cannot be tribasic; that one atom of the hydrogen at least, must be united directly with the phosphorus. Experiment shows us that in fact two atoms of hydrogen are thus directly united, the acid being monobasic. Its rational formula, therefore, is

$(H_2PO)'_H\}O$, and it may be viewed as di-meta-phosphoric acid $(PO_2)'_H\}O$, in the radical of which H_2 has replaced O. In phosphorous acid H_3PO_3, a single atom of hydrogen being united directly to the phosphorus, the other two are replaceable by basic metals, yielding acid and neutral salts, having the formulas $(HPO)''_{HR}\}O_2$ and $(HPO)''_{R_2}\}O_2$ as Rammelsberg has shown. All three hydrogen atoms may be replaced by the alcoholic radicals, forming neutral ethers; but only two atoms of this radical—those which have replaced the basic hydrogen—can be exchanged for a metal, to form salts. The third atom, replacing as it does, the alcoholic hydrogen, is still retained, forming alcoholic phosphorous acids. The constitution of these acids may be graphically represented thus:

Phosphoric acid.	Phosphorous acid.	Hypophosphorous acid.
		

Since they are formed from mono-meta-phosphoric acid by replacing hydryl by hydrogen, they resemble the phosphoric chlorhydrines, to be considered farther on.

Acid compounds of arsenic exist, corresponding to all the forms given above. Plumbic ortho-arsenite $Pb''_3(AsO_3)_2$, hydro-cupric ortho-arsenite $HCu''AsO_3$, and di-hydro-potassic ortho-arsenite H_2KAsO_3; plumbic and potassic mono-meta-arsenites, $Pb''(AsO_2)_2$ and $KAsO_2$; hydro-di-cupric ortho-arsenate HCu''_2AsO_5 (olivenite), sodic mono-meta-arsenate Na_3AsO_4, and potassic di-meta-arsenate $KAsO_3$, are examples. Antimony forms argentic ortho-sulphantimonite Ag_3SbS_3 (pyrargyrite), argentic mono-meta-sulphantimonite $AgSbS_2$ (miargyrite) and mono-meta-antimonous acid $HSbO_2$; ortho-antimonic acid H_5SbO_5, mono-meta antimonic acid H_3SbO_4, (and the salts $Pb''_3(SbO_4)_2$ and K_3SbS_4) di-meta-antimonic acid $HSbO_3$ and potassic di-meta-antimonate $KSbO_3$. The compounds of bismuth are little known. Kobellite is a plumbic ortho-sulph-bismuthite $Pb''_3(BiS_3)_2$; and di-meta-bismuthic acid $HBiO_3$ has also been obtained.

The negative radicals of the tetrad group include carbon, silicon, tin and titanium. Carbon may form

Ortho-carbonous acid	H_2CO_2	carbonic	H_4CO_4
Mono-meta	.....		H_2CO_3

Of the first, there is evidence to believe it is represented by formic acid.* Both ortho-and meta-carbonic acids form numerous salts. Calcic ortho-carbonate Ca''_2CO_4, cupric ortho-carbonate Cu''_2CO_4+aq (malachite) and hydro-tri-cupric ortho-carbonate $H_2Cu''_3(CO_4)_2$, (azurite) are examples of the former; and the common carbonates K_2CO_3, $BaCO_3$, etc., of the latter. The division of the silicates into ortho-and meta-salts, has been very clearly represented by Prof. Dana in the last number of this Journal. Ortho- and meta-stannates and titanates are well known compounds.

Of radicals having a higher equivalence, the pentads tantalum and columbium, forming a series of acids similar to quinquivalent phosphorus, and the hexads molybdenum, vanadium and tungsten, whose acids correspond to those of sexivalent sulphur, may here be mentioned.

The compounds thus far considered are derived from negative radicals; but, as already intimated, positive elements form a similar series of bodies. Since the equivalence of positive radicals rarely varies, but a single ortho-base of the same radical is known. Of ortho-bases, ortho-potassic base HKO, ortho-calcic base H_2CaO_2, and ortho-zirconic base H_4ZrO_4, are examples. The mineral pyrochroite is ortho-manganous base, H_2MnO_2 and brucite is ortho-magnesic base H_2MgO_2. From these, by the loss of the elements of water come the meta-bases, as meta-zirconic base H_2ZrO_3 but they are few in number. The perhydrates of the alkaline earths, so called, are probably meta-bases; as mono-meta-baric base H_2BaO_3 or $\left.\begin{matrix}(BaO)''\\H_2\end{matrix}\right\}O_2$, mono-meta-calcic base H_2CaO_3 or $\left.\begin{matrix}(CaO)''\\H_2\end{matrix}\right\}O_2$.

III. There is a third class of acids which is not included in either of the divisions above given. I refer to those which contain more than a single atom of the radical. Since they are derived from the ortho-acids, they are evidently meta-acids. The most familiar example is pyrophosphoric acid, $H_4P_2O_7$, derived from two molecules of ortho-phosphoric acid H_5PO_5 by the loss of the elements of three molecules of water, $H_{10}P_2O_{10}-(H_2O)_3=H_4P_2O_7$. A simple method of naming these acids is suggested by the principles already given. All acids derived from two molecules of phosphoric acid, for example, may be called di-phosphoric acids;† and the number of

* This Journal, II, xliv, 263, Sept. 1867.

† As has already been proposed by Wurtz (Chemical Philosophy, London, 1867, 159), Schiff (Ann. Ch. Pharm., IV. Suppl., 30), Naquet (Chimie, 2d ed. i, 172), Frankland (Lecture notes, 103), Rammelsberg (Chemie, Berlin, 1867, 292), (Weltzien, Syst. Uebers. der Silicate, Giessen, 1864,) and others, though in a modified

molecules of water lost, to yield the meta-acid may be indicated by a numeral prefix to the meta, as above. Hence, as pyrophosphoric acid becomes tri-meta-di-phosphoric acid. A rule for naming may be given, as follows; Prefix to the name of the acid, the numeral corresponding to the number of atoms of the negative radical contained in the formula. Then add the elements of water until the oxygen and the hydrogen atoms are equal; the numeral indicating the number of molecules of water thus employed, is to be prefixed to the word meta, placed before the name of the acid. For example, Fleitmann and Henneberg obtained two soda salts, referable to the acids $H_6P_4O_{13}$ and $H_{12}P_{10}O_{31}$. The first is a tetra-phosphoric acid, the ortho-acid of which is reproduced by adding to it seven molecules of water. The second is derived from deca-phosphoric acid, by the loss of nineteen molecules of water. Hence the salts are sodic hepta-meta-tetra-phosphate and sodic enneadeca-meta-deca-phosphate; meaning that the former is derived from four molecules of the ortho-acid by the loss of seven molecules of water, and the latter is nineteen removes from ten acid molecules. These acids and their derivatives are exceedingly numerous. Wurtz is inclined to view them as accumulated bodies, similar to the polyethylenic alcohols; stating that as PbO may be added to $\left.\begin{matrix}Pb''\\H_2\end{matrix}\right\}O_2$, producing $\left.\begin{matrix}Pb''\\Pb''\\H_2\end{matrix}\right\}O_3$ and $\left.\begin{matrix}Pb''\\Pb''\\Pb''\\H_2\end{matrix}\right\}O^4$, so to $\left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2$, $(SO_2)''O$ may be added, yielding the fuming or Nordhausen sulphuric acid $\left.\begin{matrix}(SO_2)''\\(SO_2)''\\H_2\end{matrix}\right\}O_3$ equal to $H_2S_2O_7$, our penta-meta-di-sulphuric acid. This process, however, leaves the basicity of the acid unaltered; and hence is insufficient in many cases.

The number of these acids may be illustrated by a table, showing the di- and tri-acids of the tetrad silicon, and of the pentad phosphorus, with the various meta acids derived from them, as follows:

sense. In the places above cited these authors speak of di-silicic acid, referring apparently, to any acid containing two silicon atoms. The normal di-silicic acid of these writers, however, is $H_6Si_2O_7$; whereas my di-silicic acid is $H_8Si_2O_8$, two molecules of ortho-silicic acid, from which by the loss of H_2O, is obtained $H_2Si_2O_7$, mono-meta-di-silicic acid.

	Di-acid.		*Tri-acid.*	
	Tetrad.	*Pentad.*	*Tetrad.*	*Pentad.*
Ortho,	$H_8Si_2O_8$*	$H_{10}P_2O_{10}$*	$H_{12}Si_3O_{12}$*	$H_{15}P_3O_{15}$*
Mono-meta,	$H_6Si_2O_7$	$H_8P_2O_9$	$H_{10}Si_3O_{11}$	$H_{13}P_3O_{14}$
Di-meta,	$H_4Si_2O_6$*	$H_6P_2O_8$*	$H_8Si_3O_{10}$	$H_{11}P_3O_{13}$
Tri-meta,	$H_2Si_2O_5$	$H_4P_2O_7$	$H_6Si_3O_9$*	$H_9P_3O_{12}$*
Tetra-meta,	Si_2O_4	$H_2P_2O_6$*	$H_4Si_3O_8$	$H_7P_3O_{11}$
Penta-meta,		P_2O_5	$H_2Si_3O_7$	$H_5P_3O_{10}$
Hexa-meta,			Si_3O_6	$H_3P_3O_9$*
Hepta-meta,				$H P_3O_8$

A few examples of well known compounds, formed in this way, will make the preceding remarks clear.

Cupric mono-meta-di-arsenite,	$Cu_2As_2O_5$ (Scheele's green)
Plumbic tri-meta-di-arsenate,	$Pb_2As_2O_7$
Ferric tri-meta-di-sulphate,	$Fe^{vi}S_2O_9$
Potassic penta-meta-di-chromate,	$K_2Cr_2O_7$
Penta-meta-di-periodic acid,	$H_4I_2O_9$
Di-hydro-plumbic mono-meta-tri-carbonate,	$H_2Pb_4C_3O_{11}$ (white lead).
Hepta-meta-tri-iodic acid,	HI_3O_8
Plumbic tri-meta-tetra-sulphantimonite,	$Pb_3Sb_4S_9$ (Jamesonite).
Sodic penta-meta-tetra-borate,	$Na_2B_4O_7$ (borax).
Potassic ennea-meta-tetra-iodate,	$K_2I_4O_{11}$
Ennea-meta-tetra-periodic acid,	$H_{10}I_4O_{19}$
Plumbic penta-meta-hexa-sulphantimonite,	$Pb_4Sb_6S_{13}$ (plagionite).
Magnesic ennea-meta-octo-borate,	$Mg_3B_8O_{15}$ (boracite).

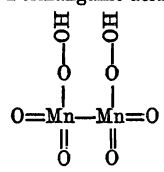
IV. In the formulas of these and similar substances the atoms of the negative radical are united to each other by oxygen, as Frankland has already shown for many of them.† It is evident, however, that these atoms may unite directly together, in which case two units of attraction in each pair of atoms will be occupied in uniting them. The equivalence of the group will then be represented by the law of saturation $E=S-2(n-1)$, already given. Certain artiads have a particular tendency to combine in this manner; as mercury in Hg_2Cl_2 and copper in Cu_2H_2; and particularly the iron group of metals, which were long supposed to be triads for this reason. Two atoms of a

* The compounds thus indicated are not distinct acids, but are multiples of the simple ortho or meta forms. See Wurtz' Chemical Philosophy, London, 1867, 158, note. It may here be remarked that monobasic phosphoric acid is capable of forming a series of polymeric compounds corresponding to the multiples given above. With silver, for example, $Ag_2P_2O_6$, $Ag_3P_3O_9$ and $Ag_6P_6O_{18}$ have been obtained. They are called di-, tri- and hexa-meta-phosphates, respectively. In the table, the first appears as tetra-meta-di-phosphate, and the second as hexa-meta-tri-phosphate.

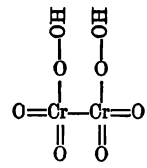
† Lecture notes for chemical students, London, 1866.

tetrad directly united, lose two bonds, and together act as a hexad. Fe_2Cl_6 or $Fe^{vi}Cl_6$ $Mn^{vi}O_3$, $Co^{vi}S_3$, $Cr^{vi}Cl_6$, etc., are examples of binaries so formed. With hydryl the compounds produced are quite numerous, and many of them occur as minerals. Thus ortho-ferric base $H_6Fe^{vi}O_6$ is limonite, and ortho-aluminic base $H_6Al^{vi}O_6$ is gibbsite. From these are derived the meta-bases; as from $H_6Al^{vi}O_6$ comes $H_4Al^{vi}O_5$ mono-meta-aluminic base, and $H_2Al^{vi}O_4$ di-meta-aluminic base, diaspore. So from limonite $H_6Fe^{vi}O_6$ may be obtained $H_4Fe^{vi}O_5$ mono-meta-ferric base (xanthosiderite) and $H_2Fe^{vi}O_4$ di-meta-ferric base (Göthite). Manganite $H_2Mn^{vi}O_4$ is di-meta-manganic base. Permanganic and perchromic acids, $H_2Mn_2O_8$ and $H_2Cr_2O_8$, as was stated on page 389, must contain their radicals as heptads, if their atoms are united by oxygen. Frankland, however, to avoid a violation of the fundamental law of saturation, supposes that the manganese and chromium atoms are directly united, and makes an oxygen atom intervene between each negative atom and the hydryl, thus :—

Permanganic acid.



Perchromic acid.



On either supposition, their constitution is anomalous.

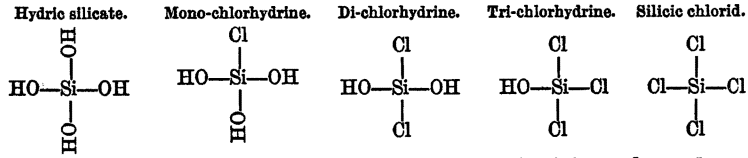
The same direct union takes place with the carbon group of tetrads forming $C^{vi}Cl_6$, $Sn^{vi}O_3$, $Ti^{vi}N_2$, etc. With hydryl, therefore, such a series of compounds as the following, becomes possible.

	Carbon.	*Silicon.*
Ortho-oxalic acid,	$H_6C^{vi}O_6$	$H_6Si^{vi}O_6$
Mono-meta-oxalic acid,	$H_4C^{vi}O_5$	$H_4Si^{vi}O_5$
Di-meta-oxalic acid,	$H_2C^{vi}O_4$	$H_2Si^{vi}O_4$
Di-carbonic tri-oxyd,	$C^{vi}O_3$	$Si^{vi}O_3$

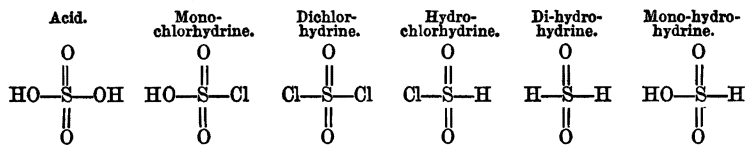
In the carbon series, the di-meta form is ordinary oxalic acid, from which the group may be named. The ortho-oxalic acid is represented in plumbic ortho-oxalate $Pb''_3C^{vi}O_6$ but the mono-meta acid seems to be unknown. The silicon compounds do not appear to be known with certainty, although several observers have reported the discovery of a di-silicic tri-oxyd (sesquioxyd of silicon) with some of the hydrates belonging to it.

The view which has now been given, of the constitution of acids and bases, renders very simple the relation of these bodies to the chlorhydrines, so-called. An acid being converted into

a chlorhydrine by exchanging its hydryl (HO)′ for the monad chlorine (from which fact the word chlorhydrine comes) it is evident that there may be as many chlorhydrines obtained from a given ortho or meta acid, as is equal to the number of atoms of its basic hydrogen, less one, the final product being the chlorid of the radical. Thus with ortho-silicic acid, there may be



Compounds corresponding to all these chlorhydrines, have been obtained by Friedel and Crafts.* If the acid be a meta-acid, the radical is partially saturated by oxygen, and the final result is a so-called oxychlorid (the chlor-aldehyd of Odling); the true aldehyd being a similar body, containing hydrogen in place of chlorine. For example, di-meta-sulphuric acid may form in this way the following bodies:



A comparison of these formulas with those of hypophosphorous and phosphorous acids on page 392, will make clear the relation of these acids to mono-meta-phosphoric acid, by showing that they are its hydro-hydrines, the last of the series, H_3PO phosphoric aldehyd, not being yet known.

The results given in the foregoing pages may be briefly recapitulated. I have attempted to show:

1. That all the bonds of any simple radical may be saturated by the monad hydryl.

2. That the compounds thus formed, are determined by the electro-chemical character of the radical; being acids when it is negative, and bases when it is positive.

3. That acids and bases so formed, being evidently normal, are conveniently designated by the prefix *ortho.*

4. That the equivalence of negative radicals varies through several stages, while that of positive rarely changes. And hence, that there may be a series of ortho acids from a given negative radical, but only a single base from a positive one.

5. That by the removal of the elements of water from a normal or ortho acid, a derived acid is produced, which may be indicated by the prefix *meta.*

* This Journal, II, xliii, 155, March, 1867.

6. That when there are several such derivatives, the Greek numeral prefixes di, tri, tetra, etc., may be used to indicate the number of molecules of water removed from the ortho acid to yield the meta-form.

7. That intermediate between the simple ortho- and meta-acids, are others containing more than a single atom of the negative radical; and that these acids may be designated by di, tri, tetra, etc., (according to the number of negative atoms) prefixed to the name of the acid, while the number of molecules of water removed from a multiple of the normal acid to form them is indicated by the same numerals prefixed to the meta.

8. That while the negative atoms in the compounds just mentioned are united by oxygen, there may be other compounds whose negative or positive atoms are united directly; thus producing a fourth class of acids and of bases.

By classifying thus the substances known as acids and bases, —and of course the salts derived from them—it is hoped that their relations to each other may be made clearer. And by giving them systematic names, their position in the series may be fixed, and a step be taken toward the establishment of a rational nomenclature.

New Haven, Oct. 10, 1867.