

THEORIES of ACIDS.

and especially

THE BASICITY of ACIDS.

By Miss Edith Perkins

Class of 1900



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The ancients possessed very little knowledge of the acids--acetic acid in the form of vinegar being, in fact, the only one known to them, and its solvent power was greatly overrated. Among the Arabists, ~~acids~~ acids were better and more widely known. Basil Valentine speaks of the preparation of nitric acid from salt petre and sulphuric acid as a very old process. He himself obtained sulphuric acid by heating green vitriol and pebbles; and in this same way, he made "spiritus salus" (hydrochloric acid) by heating green vitriol and common salt. Aqua regia was known to both Geber and Valentine. Oil of Vitriol was highly valued, being regarded as the "sulphur philosophorum", and it was thought, might lead to the discovery of the "materia prima".

From the time of Lavoisier, Chemistry took its place among the sciences, and to the "Father of Chemistry" we owe much of our present knowledge. Lavoisier and Berzelius believed that the properties of acids depended upon their containing oxygen, and that oxygen was, therefore, an unfailing constituent of all acids. When Cavendish discovered that water was formed upon burning hydrogen, Lavoisier at once saw the way to the fulfilment of his oxygen theory. He claimed that the hydrogen came from the water; that the oxygen was fixed in the metal; and hence it was the metallic oxide, not the metal that was dissolved by the acid. He says--"The combustible body, is, as a rule, converted into an acid by its combination with pure air, but the metals, on the contrary, into metallic calces. For him, sulphuric, phosphoric, and nitric acids, consisted of sulphur, phosphorous, salt petre gas (NO) and oxygen. For him, too hydrochloric acid consisted of oxygen com-



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bined with the radical "muriatique"; the chlorine liberated by its oxidation was regarded as oxidized hydrochloric acid.

The theory of oxygen acid was abandoned in the second decade of this century by most chemists. The discovery of the alkali metals by Davy, and the allied researches on the elementary nature of chlorine were the starting points in its downfall. These alkalies were supposed to be elements, though from the time of Lavoisier it was considered probable that their constitution was analagous to the metallic oxides, and that therefore, they were oxygen compounds. At last, Davy separated them by using the electric current. His correct assumption that the metals, separated at the negative pole, were true elements, did not find immediate acceptance. In fact, he himself thought they might contain hydrogen, especially after its presence in the alkalies had been proven by Gay Lussac and Thenard. This idea crept in from an analogy with ammonia, which was supposed to contain oxygen, that was drawn from it in the foundation of ammonium amalgam. This wrong conclusion was set right by Gay Lussac and Thenard.

At the time when Davy, Gay Lussac, and Thenard began their investigations, hydrochloric acid gas was supposed to hold chemically combined water. But the most powerful reducing agents were unable to prove the presence of oxygen, either in hydrochloric acid or chlorine, and this of itself made them think chlorine an element, and hydrochloric acid its hydrogen compound. So "Hydrogen and chlorine unite to form anhydrous hydrochloric acid, which is decomposed by sodium, with liberation of one-half its volume of hydrogen, and the formation of sodium chloride, which latter also results directly from the combination of sodium and chlorine." Upon these grounds, Davy declared Chlorine an element, and so named it. Gay Lussac and Thenard at last agreed with



him.

Berzelius, always cautious about accepting new theories, refused to accept this new idea. But he soon admitted that sulphuretted and telluretted hydrogens, were hydrogen acids. He dogmatically held that chlorine, fluorine, and iodine contained oxygen, till his own work on ferrocyanogen and sulphocyanogen agreed with the theory of non oxygenated acids. At last, in 1825, he gave up, although he still distinguished sharply between haloid and amphoteric salts.

From the fact that iodic anhydride lacked acid properties but acquired them after combination with water, Davy saw that hydrogen not oxygen was the acidifying principle, and hydrogen, in his opinion, was the necessary principle of all acids.

Dulong said oxalic acid was composed of hydrogen with carbonic acid, and its salts were an analogous combination of metals with the elements of carbonic acid. In these discussions, a dualistic conception of acids and salts was still apparent, hydrogen and the metals being placed opposite the salt forming radicals; but the way was now opened for a unitary theory of acids and salts.

Berzelius still held to the dualistic view, and laid special weight upon the possibility of preparing the immediate constituents of the acids--the radicals of the hydrogen acid theory being but seldom capable of isolation.

Daniell put forth this argument in favor of the views of Dulong and Davy:---"When galvanic currents are passed through different electrolytes, e. g., acidified water, fused chlorid of platinum or a solution of potassium sulphate, amounts of hydrogen, platinum, or potassium are set free at the negative pole, which stand to one another in the proportions of the chemical equivalent numbers." This agrees with



Farraday's Electrolytic Law, with the exception of potassium sulphate, when an equivalent of hydrogen is liberated in addition to an equivalent of base. The current therefore, appears to do double work, in spite of the law just mentioned. The apparent contradiction is done away with by accepting the view of Davy and Dulong, i. e., by assuming potassium as positive and the radical  $\text{SO}_4$  as negative. The conclusion drawn from this observation on the constitution of salts was then extended to acids---hydrogen as one constituent, and a radical (containing oxygen or not- as the other.

Gay Lussac and Gmelin thought the atoms of the various metallic oxides contained one atom of oxygen to one atom of metal, and combined with one atom of acid to form neutral salts. But this theory, according to which almost every acid was regarded as monobasic, could no longer hold its ground after Graham's famous investigation of the phosphoric acids.

Previous work on phosphoric acid ( $\text{P}_2\text{O}_5$ )<sup>#</sup> had indicated isomeric conditions which showed very different salts. The difference was noted in the precipitation of silver salts from ordinary and from pyrophosphoric acids. Every one knew the difference in the amount of water in the compound, but water of crystallization did not count for much, so the anhydride was still regarded as the acid.

Graham cleared up the modifications of phosphoric acid. He says-- "The distinctive character of phosphoric acid which exists in common phosphate of soda, as compared with the other modifications, is a disposition to form salts which contain three atoms of base to the double atom of acid."

"Pyrophosphoric acid is disposed to form salts having two atoms of base. Such salts of the preceding acid as contain no more than two



atoms of fixed base, pass into pyrophosphates when heated to redness."

Metaphosphoric acid is disposed to form salts which contain one atom of base to the double atom of acid. The other modifications pass into metaphosphoric acid when heated to redness per se, or in contact with no more than one atomic proportion of fixed bases, as sodium."

It is a matter of certainty that if we take one combining proportion of any modification of phosphoric acid, and fuse it with sodium or sodium carbonate, we shall form a metaphosphate, a pyrophosphate, or a phosphate, according as we use one, two, or three proportions of of base. The acid when separated from the base will possess and retain for some time the characters of its peculiar modification. It would appear therefore that the acid is impressed with a disposition to form different classes of salts by the proportions of base to which it has been united, and that it retains this disposition even when liberated from the original compound. But probably the modifications of the phosphoric acids when in what we call a free state, are still in combination with their usual proportion of base and that that base is water.

Phosphoric acid----- $H_3P$ --terphosphate of water.

Pyrophosphoric acid- $H_2P$ --biphosphate of water.

Metaphosphoric acid- $H_1P$ --phosphate of water.

Now when one of these compounds is treated with a strong base, the whole or a part of the water is supplanted, but the amount of base in combination with the acid remains unaltered.

The conclusion Graham draws are:--"

I. Acids contain a certain number of hydrogen atoms, through replacement of which, salts are formed.

II. A molecule of acid is not necessarily, or even commonly equivalent to a molecule of base. That is some acids, as phosphoric acid, have a



varying basicity."

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Liebig followed up Graham's work and showed that the various organic acids resemble the phosphoric acids in basicity. He denied that the atoms of all acids are equivalent to one another, and gave as the criterion of a polybasic acid its capacity of forming compound salts with different metallic oxides. Liebig was the first to distinguish between mono, di, and tribasic acids. He criticized the different properties we ascribe to water --that of basic, entering into the composition of salts, water of crystallization, etc.-- and all because we wish to distinguish between haloid and proper salts-- a distinction that does not exist in the salts themselves which are similar.

Liebig's views on acids are essentially correct today. They are as follows:--

- I. " Acids are hydrogen compounds in which the hydrogen is replaceable by a metal."
- II. "Neutral salts are those compounds in which all the hydrogen has been replaced by its equivalent of metal. Most so called anhydrous acids act only in the presence of water or at a higher temperature."
- III. "On neutralization of acids by metallic oxides (bases) hydrogen is generally eliminated in the form of water. Whether this water comes from the acid or the base is immaterial."
- IV. "The part to be emphasized is that there is generally no salt formed without the formation of water, and that of acids. The principle to be borne in mind is that the saturation capacity of acids depends on the amount of hydrogen; if we call all except the hydrogen of the acid, the acids radical, oxygen need not be present in this radical.



Liebig did much valuable work in the organic acids. In 1837, he, in conjunction with Dumas, published an article "On the Constitution of Several Polybasic Acids." The following table shows how they regarded citric acid:---

Citric Acid -----

Absolute Citric Acid:----- $C_{12}H_5O$

Anhydride in combination

with bases.

Dry Acid----- $C_{12}H_5O_{11}, 3HO.$

Crystallized Acid----- $C_{12}H_5O_{11}, 2HO$  2aq

Barium Salt ----- $C_{12}H_5O_{11}, 3Ba O$

Sodium Salt -----  $C_{12}H_5O_{11}, 3Na O$

Silver Salt -- -----  $C_{12}H_5O_{11}, 3AgO$

They refused to accept Berzelius' opinion that tartaric acid contained  $C_4H_2O_5$ , and they thought it capable of losing water at the expense of its constituents. "In the formation of citrates, tartrates, meconates, and cyanurates, each oxygen atom contained in the base which combines with the acid, replaces and eliminates in the form of water, an atom of oxygen contained in the acid; hence, these acids do not form salts with an excess of base, but salts of the same description as those of phosphoric acid."

In 1838, Liebig "On the Constitution of the Organic Acids" accurately describes meconic acid as tribasic and comenic acid as bibasic, in accordance with the views, at present accepted.

The work on lactic acid is quite characteristic, and affords a good example of the working out of the organic acids.







Kolbe now regarded proprionic acid and lactic acid as derivatives of carbonic acid---



He said that dibasic acids form neutral and acid salts or ethers, monobasic amido acids and diamides; that lactic acid does not, that for ascertaining the saturating capacity of an acid, the salts of tin or other heavy metals were quite appropriate, that Wurtz's ethyl lactate was the ethyl ether of oxyethyl proprionic acid, etc. He was right; lactic acid is hydroxy-proprionic acid, but he missed its relation to propyl glycol; the idea did not strike him that glycols are alcohols of dyad radicals.

Lactic acid contains two typical or extra radical hydrogen atom of the monobasic acid; while the second may be exchanged for acid radicals, like that of the alcohols. Lactic acid is at the same time, a monobasic acid and an alcohol; it is proprionic acid, in which one hydrogen atom of the ethyl is replaced by hydroxyl, and its formula is therefore  $C \begin{smallmatrix} H \\ 2 \quad 4 \end{smallmatrix} (O H) C O.OH$