

**ALEMBIC CLUB REPRINTS, NO. 10;
RESEARCHES ON THE
ARSENIATES, PHOSPHATES, AND
MODIFICATIONS OF
PHOSPHORIC ACID**

Published @ 2017 Trieste Publishing Pty Ltd

ISBN 9780649195398

Alembic Club Reprints, No. 10; Researches on the arseniates, phosphates, and modifications of phosphoric acid by Thomas Graham

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THOMAS GRAHAM

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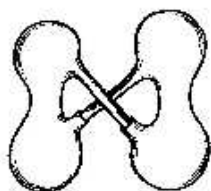
BY
THOMAS GRAHAM, F.R.S.
(1833)



Edinburgh
THE ALEMBIC CLUB

Chicago
THE UNIVERSITY OF CHICAGO PRESS

1912



PRINTED IN GREAT BRITAIN BY
OLIVER AND BOYD, EDINBURGH

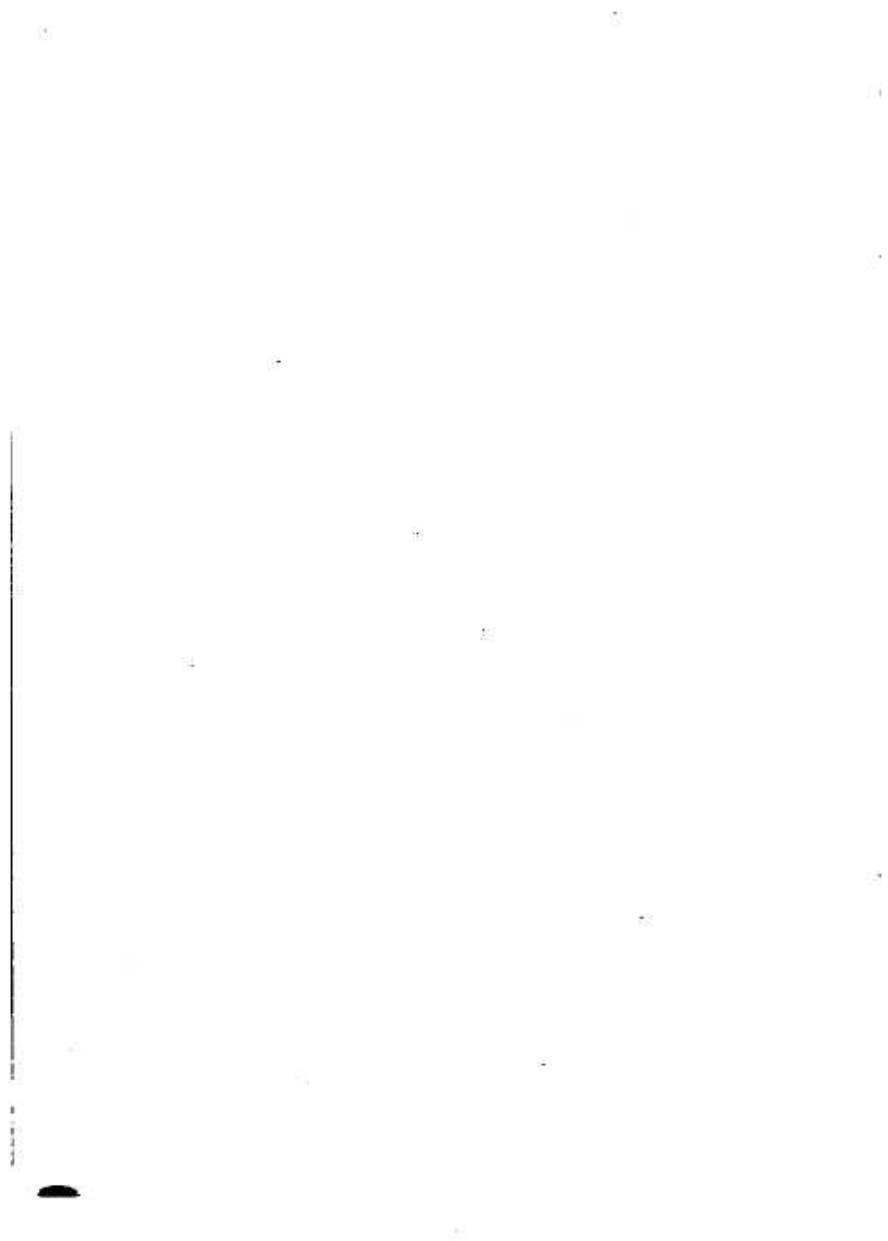
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P R E F A C E.

THE important paper reprinted here is admittedly the most valuable contribution made by Graham to pure chemistry. From the historical point of view, it is specially noteworthy on two different grounds—firstly, because in it the relations to each other of ortho-, pyro-, and metaphosphoric acids and the corresponding salts were first pointed out; and secondly, because it formed the starting point of the idea of the Basicity of Acids—an idea which undoubtedly originated with Graham.

For the guidance of readers to whom the old-fashioned nomenclature of the paper may be unfamiliar, it may be explained that "subsesquiphosphate" or "subphosphate" corresponds to normal orthophosphate; while "phosphate" or "neutral phosphate" is applied to such salts as $\text{Na}_2\text{HPO}_4, 12\text{H}_2\text{O}$, and "biphosphate" to such salts as $\text{NaH}_2\text{PO}_4, \text{H}_2\text{O}$. The notation of the paper is the dualistic system introduced by Berzelius—each dot placed above a symbol representing an atom of oxygen, with which the atom for which the symbol stands is supposed to be combined directly. The formulæ are based upon the old atomic weights.

L. D.



RESEARCHES
ON THE
ARSENIATES, PHOSPHATES,
AND
MODIFICATIONS OF PHOSPHORIC
ACID.*

Received January 29. Read June 19, 1833.

I. *Of the Subsalts.*

NO classes of salts have more liberally rewarded investigation than the arseniates and the phosphates. Witness the discovery of the extraordinary phosphates of lime by BERZELIUS; the observation of the identity of form of the corresponding arseniates and phosphates by MITSCHERLICH, and the doctrine of isomorphism to which that observation led; the discovery by the same chemist of two biphosphates of soda, agreeing in composition but differing in form; and lastly, the discovery of the pyrophosphates by my friend and townsman Mr. CLARK. Much, however, still remains to be done to complete the history of these interesting salts.

1. *Subarsenate and Subphosphate of Soda.*

The extraordinary disposition of arsenic and phosphoric acids to form subsesquisalts—such as the brown arseniate and the yellow phosphate of silver, the common

* [From "Philosophical Transactions" for 1833, pp. 253-284.]

subarseniates of lime, lead, &c.—is well known. Corresponding alkaline salts exist, which merit the consideration of chemists.

To a strong solution of arseniate or phosphate of soda add a solution of caustic soda till the liquor feels soapy between the fingers. At least half as much soda as already in the salt must be added, but an excess of alkali is not injurious. Concentrate the liquor till a pellicle forms on its surface, and then allow the solution to cool. At the temperature of 150° , tufts of slender prismatic crystals appear in it; these rapidly increase in quantity, and finally fill the vessel. The crystals must be drained as well as possible, and the mother-liquor may be thrown away, as it contains little else than the excess of caustic soda and the soluble impurities of the salts. It is necessary, without loss of time, to redissolve the crystals in twice their weight of hot water, to filter the solution through paper, and to recrystallize.

Both salts crystallize readily, as their solutions cool, in the form of six-sided prisms, which are generally slender. The prism is often terminated by a flat surface, which appears to be a right section. The angles of the crystals were not measured, but two of them are much more obtuse than the remaining four. The subarsenate may be procured in crystals of larger size than the subphosphate, but of the same form. These salts in the crystalline form are not altered by exposure to the air, but in solution they absorb carbonic acid; and when again crystallized, a portion of carbonate is found to adhere pertinaciously to the crystals. It is easy, however, to produce fine crystals by the process described, free from carbonic acid, and apparently pure.

A solution of the subarsenate is precipitated exactly neutral, by an excess of fused nitrate of silver, the brown subarsenate of silver falling down, which proves the

alkaline subarsenate to be in the same state of neutrality as the metallic subarsenate, and consequently of a similar constitution. The subphosphate gives, with the same reagent, the yellow subphosphate of silver, and leaves a liquid either neutral or very faintly alkaline by the most sensible cudbear paper. The alkalinity, however, must be accidental, as it disappears on the addition of the smallest quantity of acetic acid. These salts, therefore, rank as subsesquisalts, containing one proportion and a half of base to one of acid.* They are interesting as the only known soluble salts of that constitution. The subphosphate had been previously crystallized by Dr. DALTON and recommended as a reagent; † but it was supposed to contain twice as much soda as the common phosphate. MITTSCHERLICH also infers the existence of a subsesquiphosphate of soda, from the quantity of carbonic acid expelled, when phosphate of soda is calcined with carbonate of soda. ‡ The same salt appears likewise to have fallen into the hands of Dr. THOMSON, as an accidental product, but is described as a carbonophosphate of soda, being probably impure. §

In regard to the properties of these salts. They are strongly alkaline to the taste, and act upon chlorine and iodine like free alkalis. Indeed the excess of their alkali is separated by the weakest acids, even by carbonic acid, and the common rhomboidal phosphate or arseniate afterwards appears on crystallizing. When the pure crystals are thrown into neutral nitrate of ammonia, the volatile alkali is disengaged. At 60° FAHR. 100 parts

* Three atoms oxygen in the base for five atoms oxygen in the acid.

† Manchester Memoirs, N.S., vol. iii. p. 12.

‡ Annales de Chimie et de Physique, tom. xix. p. 363.

§ First Principles, &c., vol. ii. p. 451.