

Dec. 17, 1849.

The PRESIDENT in the Chair.

The following presents were announced :

“The Pharmaceutical Journal,” for December, from the Editor.

“The Journal of the Franklin Institute,” for October, from the Institute.

A. Völker, Ph. D. was duly elected a Fellow of the Society.

The following Papers were read :

“On Titanium,” by Professor Wöhler, (Vol. II. p. 352).

II.—*On the Action of Sulphur upon the Pentachloride of Phosphorus.*

BY J. H. GLADSTONE, PH. D. F.C.S.

The object of the present communication is to describe a substance, which was first noticed by me during my researches upon the compounds of the halogens with phosphorus, but, on account of its very distinct character, was reserved for separate consideration. I found, that when sulphur and pentachloride of phosphorus are mixed together, and heat applied, combination takes place; a mass of colourless crystals is formed, which, if the heat be continued, are converted into a yellow liquid, that may be distilled, and obtained pure by repeating the distillation. This liquid contains phosphorus, chlorine, and sulphur, but differs from the sulphochlorides of phosphorus already known, both in physical and chemical properties. Attempts to analyze the new substance, by oxidizing it with nitric acid, failed, because the heat evolved during the reaction volatilized part of the liquid. The results, however, appeared to indicate that the sulphur and phosphorus were in the proportion of 4 to 1; and this led me to the best method of preparing the compound, which is as follows.

Three parts of pentachloride of phosphorus are mixed in a small retort with 1 part of sulphur; that is, 1 equiv. of the former to rather more than 4 equivs. of the latter, and combination is deter-

mined by heating the mixture till it begins to fuse. There are then formed in the retort a yellow liquid, and a mass of transparent, colourless crystals, differing in appearance from the pentachloride of phosphorus. A gentle heat must be maintained until this transformation has taken place throughout the whole mass, when the crystalline body will be found gradually to disappear, and the liquid to increase in quantity. On cooling, the crystals are reproduced; but if the liquid be briskly boiled, a distillate will be obtained, from which only a small quantity of crystals separates. A transformation has thus been effected; for the whole liquid may be distilled over, the thermometer, which at first indicated about 110° C. (230° F.) gradually rising; and nothing remains in the retort, except perhaps a small quantity of a peculiar dark-coloured viscid matter, which will be immediately described.

If a smaller proportion of sulphur be employed, the same products result; but unaltered pentachloride of phosphorus is found in the retort after distillation.

If, on the contrary, a larger proportion of sulphur be mixed with the pentachloride of phosphorus, both substances are likewise produced; but, during the distillation of the yellow liquid, it assumes a deep colour, and there remains in the retort a dark brown mass. This is a mixture of sulphur with another substance, which may be distilled by the heat of a spirit-lamp. It is of a viscid consistence; water has no effect upon it, but alkalis appear to separate some chlorine. I believe it to be a secondary product, resulting from the action of sulphur upon the new liquid itself at an elevated temperature.

Under no circumstances have I remarked the least trace of dichloride of sulphur, free chlorine, or any other product accompanying the reaction just described. The crystalline and the liquid body are found in various proportions, and sometimes there remains scarcely any amount of crystals. Thus it would appear, that the liquid at least is formed by the direct combination of sulphur with the pentachloride of phosphorus.

LIQUID COMPOUND.

No method of rectifying the liquid compound with perfect accuracy has presented itself to me. The crystalline body will rise in vapour along with it; but an approximate separation may be effected by decanting the liquid from the crystals, and submitting it to gentle

distillation. That which passes over first must be redistilled until a product is obtained, which boils uniformly at a temperature not exceeding 125° C. (257° F.).

The substance thus prepared is a clear mobile liquid, of rather high refracting power, heavier than water, of a pale yellow colour, and possessing an odour somewhat acid, but not powerful. It evaporates at ordinary temperatures, and shows great disposition to rise in vapour, when heated. This and other causes have combined to prevent my determining its boiling point within a degree or two, but it is about 118° C. (244.4° F.). It showed no disposition to fuse when immersed in a mixture of ice and common salt, at a temperature of -17° C. (1.4° F.). It is capable of dissolving a large amount of sulphur when hot, which it deposits again in crystals of the form of rhomboidal octohedrons, or sometimes in needles. It also dissolves phosphorus, almost to an unlimited extent when hot, and deposits that substance also on cooling in a crystalline form. The same may be said of the pentachloride of phosphorus. The new liquid under consideration dissolves iodine, imparting a deep red colour to the solution, as is the case with most of these liquid compounds of phosphorus and the halogens. It mixes with bisulphide of carbon. Strong sulphuric acid has no action upon it, at least in the cold; and instead of dissolving in ether, alcohol, or oil of turpentine, it violently attacks these organic solvents.

The new liquid is not affected by hydrogen gas, either at the ordinary or boiling temperature; but if a stream of hydrosulphuric acid be passed over it, sulphur separates, bubbles of gas rise through the liquid, and another liquid compound remains. Metals decompose the substance under consideration, in some cases with, in other cases without the assistance of heat. It is violently oxidized by nitric acid. When it is brought into contact with water, decomposition instantly commences; the characteristic odour of sulphochloride of phosphorus is perceptible; and after a few hours, there remains a quantity of sulphur, contaminated with some sulphide of phosphorus, and in solution, hydrochloric, sulphuric, phosphoric, and perhaps phosphorous acid, together with another acid containing both phosphorus and sulphur, and giving a brown precipitate with nitrate of silver, not soluble in dilute nitric acid, but slightly so in ammonia. I believe this to be the sulphonyphosphoric acid described by Wurtz,* notwithstanding the remark of that chemist, that the silver-salt is

* Ann. Chim. Phys. [3], XX, 372.

too unstable to be prepared. The same decomposition results, only more rapidly, when solutions of the alkalis are employed; in that case, however, the liquid, before being entirely destroyed, assumes a dark red colour, and the sulphur which separates is mixed at first with flocculent masses, of an orange tint. A remarkable circumstance attending this reaction is the total absence of hydrosulphuric acid among the numerous resulting compounds, unless the solution be boiled, in which case it probably arises from decomposition of the sulphyphosphoric acid.

It appeared to me that this decomposition by water might be taken advantage of for the ultimate analysis of the compound, provided means could be devised for completely separating the phosphorus, sulphur, and chlorine existing under so many different forms. The following process I found effectual:—The liquid, having been weighed, was decomposed by a dilute solution of ammonia, in a corked flask, so as to prevent loss of the liquid by evaporation. When the decomposition was complete, nitrate of silver was added, which produced a dark brown precipitate, and rendered the ammoniacal solution of an inky appearance. This was boiled briskly for some minutes, until the precipitate completely separated, leaving a clear supernatant liquid. The black precipitate was then collected, well washed with ammonia, and afterwards oxidized by means of strong nitric acid. If pure sulphur separated, it was collected by itself. The nitric acid solution thus obtained was added to the previous ammoniacal solution; the chloride of silver was recovered by completely acidifying the liquid by additional nitric acid if necessary, and the sulphuric and phosphoric acids were estimated by baryta. It was found necessary to continue the boiling of the ammoniacal solution for several minutes, or the whole amount of chlorine was not converted into silver-salt.

I. 0·3765 grm. of the new liquid yielded 0·988 grm. of chloride of silver, 0·059 grm. of free sulphur, 0·222 grm. of sulphate of baryta, and 0·1047 grm. of phosphoric acid.

II. 0·1882 grm. of a separate preparation yielded 0·253 grm. of sulphate of baryta, and 0·0494 grm. of phosphoric acid, besides 0·010 grm. of free sulphur.

III. 0·788 grm. of a separate preparation, having a somewhat higher boiling-point, yielded 2·041 grms. of chloride of silver, 1·001 of sulphate of baryta, and 0·068 grm. of phosphoric acid, besides 0·130 grm. of free sulphur, which proved, however, to contain phosphorus.

IV. 0.254 grm. of the new liquid was analyzed in a totally different manner. It was poured into a flask containing reduced copper, which was corked up until the odour of the liquid had entirely disappeared. The resulting mass was exhausted with hot water, and afterwards oxidized by nitric acid. Owing to the formation, I imagine, of dichloride of copper, the chlorine was in a great measure contained in that portion which was subjected to the action of nitric acid; hence an almost inevitable loss. However, it yielded 0.6265 grm. of chloride of silver, equivalent to 60.84 per cent of chlorine. The sulphate of baryta obtained was 0.451 grm.

V. 0.4175 grm. was analyzed in the same manner as the last, iron being employed in place of copper. The application of heat was necessary to effect the decomposition. 0.521 grm. of sulphate of baryta was obtained, and 0.031 grm. of free sulphur.

These results reckoned to 100 parts are :

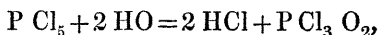
	I.	II.	III.	IV.	V.
Phosphorus . . .	12.3	11.7	{ 37.8 }	—	—
Sulphur . . .	23.8	23.8		24.5	24.6
Chlorine . . .	64.7	—		—	—

These numbers accord sufficiently with these deduced from the formula PS_4Cl_5 .

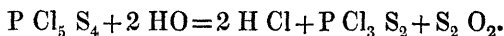
Phosphorus . . .	11.70
Sulphur . . .	23.40
Chlorine . . .	64.90
	<hr/>
	100.00

Several views may be taken of the rational constitution of this new liquid compound. It may be considered as a double chloride of phosphorus and sulphur; thus, $\text{P Cl}_3, 2 (\text{S}_2 \text{Cl})$; but the action of water upon the substance appears to assimilate it to those compounds in which phosphorus is combined with five atoms of halogen, two of them being easily replaceable by sulphur or oxygen. We may regard it, therefore, as $\text{P Cl}_3 \text{S}_2, 2 (\text{S Cl})$, and suppose the sulphochloride set free by the decomposition of the chloride of sulphur;—or as pentachloride of phosphorus in direct combination with four atoms of sulphur; $\text{P Cl}_5 \text{S}_4$. This is the view I prefer, and I shall accordingly designate the new liquid as sulpho-perchloride of phosphorus. The manner in which water acts upon this compound will then appear

analogous to its mode of action upon the pentachloride of phosphorus itself; that is, two atoms of hydrogen remove two of the five atoms of chlorine; but the two atoms of oxygen thus liberated, instead of entering into the composition of the new substance, combine in this case with two of the atoms of sulphur, leaving the other two still to form part of the phosphorus compound.



and



The existence of hyposulphurous acid in the solution is hypothetical; and I must remark that, where a considerable amount of water was employed, I never observed sulphurous acid among the products, even when the decomposition was effected by means of dilute acid. But, unless in large quantity, the odour would be masked by that of the sulphochloride, and there are many conceivable ways in which the sulphurous acid might be immediately reduced or oxidized. Yet, upon adding a very small quantity of water to a portion of the liquid in a corked tube, a strong pungent odour was observed when the cork was removed, and the gas produced a blue colour when suffered to fall upon a mixture of starch and solution of iodate of potash. We may, therefore, conclude that sulphurous acid was evolved.

I may here observe that sulphochloride of phosphorus, prepared in the manner described by Serullas, and decomposed by water or solutions of alkalis, without the aid of heat, gives the acid formerly referred to, which yields a brown silver-salt, and not a trace of hydro-sulphuric acid.

The view which regards the liquid just examined as a direct compound of sulphur with the pentachloride of phosphorus, receives additional support from the discovery of Kremers, who has recently shown* that sulphurous acid combines directly with pentachloride of phosphorus, giving rise to two liquids, each resolvable by water into sulphurous acid, with phosphoric and hydrochloric acids. These he terms sulphites of the pentachloride of phosphorus, with the formulæ $\text{P Cl}_5, 2 \text{SO}_2$, and $\text{P Cl}_5, 3 \text{SO}_2$. Rose's sulphate of the pentachloride of phosphorus is a substance about which too little is accurately known to warrant us in drawing any deductions from it.

* Ann. Ch. Pharm. June, 1849.

SULPHUR UPON THE PENTACHLORIDE OF PHOSPHORUS. 11

In order to ascertain whether another compound, of different formula, could be obtained from the liquid under examination, by merely collecting that which rose first in vapour, I subjected a portion for some time to a temperature not exceeding 100° C. The portion which evaporated, condensed into a clear yellow liquid, apparently identical with that formerly examined. 0.385 grm. analyzed as above, yielded 1.020 grms. of chloride of silver; the estimation of sulphur and phosphorus was unfortunately lost.

This number, reckoned to 100 parts, gives .

Chlorine = 65.35 per cent ;

a result sufficient to prove the identity of this liquid with the previously-described sulpho-perchloride of phosphorus.

Through the kindness of Messrs. Watts and Russell, I am enabled to add a determination of the specific gravity of the vapour of sulpho-perchloride of phosphorus. The details of the experiment are as follows :

Weight of globe filled with air, at temp. 14.5° C. } 944.10 grs.
(58.1° F.) ; bar. press. 29.64 inches.

Weight of globe filled with vapour, at temp. 203° C. } 951.60 grs.
(397.4° F.) ; bar. press. 29.87 inches.

Capacity of globe 29.15 cub. in.

Volume of residual air, at temp. 13° C. (55.4° F.) ; } 9.82 cub. in.
bar. press. 29.77 inches.

The specific gravity of the vapour, calculated from these numbers is 5.5. Now, if we suppose 6 volumes of the vapour of pentachloride of phosphorus to unite with 4 volumes of sulphur vapour without condensation, we obtain the theoretical density 5.552. This would, therefore, appear to be the specific gravity of the vapour in question.

CRYSTALLINE COMPOUND.

It has already been observed, that the first distillates in the preparation of sulpho-perchloride of phosphorus deposit crystals on cooling. These will often not appear till after the lapse of several hours, or even days. In such a case, they are usually perfectly transparent and well defined, having the form of two octagonal pyramids, placed base to base, and the projecting angle at the point of juncture truncated, so as to form hexagons. The crystals thus obtained, unquestionably

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sometimes contain pentachloride of phosphorus; but they comport themselves in contact with water, in a manner similar to the liquid compound just described.

I. 0.2945 grm. of well-defined crystals, drained, and exposed for awhile to a current of dry air, having been analyzed according to the process formerly described, yielded 0.964 grm. of chloride of silver, and 0.110 grm. of sulphate of baryta.

II. 0.1945 grm. of a separate crystallization, also well-defined and uniform, which was drained, and dried by means of asbestos, yielded 0.6415 grm. of chloride of silver, and 0.058 grm. of sulphate of baryta.

These numbers, reckoned to 100 parts, are :

	I.	II.
Phosphorus (by difference)	14.1	14.6
Chlorine	80.7	81.3
Sulphur	5.2	4.1

The proportion between the phosphorus and chlorine is evidently as 1 : 5, which would require :

	I.	II.
Phosphorus	14.6	14.7
Chlorine	80.7	81.3

We can scarcely suppose these crystals to be anything else than pentachloride of phosphorus, contaminated with a small quantity of the sulpho-perchloride ($\text{P Cl}_5 \text{ S}_4$), which could not be easily removed. Yet, in other analyses, where the crystals were so well defined, I have found a larger amount of sulphur; in one instance as much as 16.6 per cent. This leads me to believe either that a crystalline compound of sulphur with the pentachloride of phosphorus does exist, or that the sulpho-perchloride has itself a great tendency to cohere to the pentachloride of phosphorus. It is on this account alone, that I have specially described the crystalline body.

Remarks on the use of the Alkaline Carbonates, for the prevention of Incrustation in Steam Boilers.

By MR. ALFRED ANDERSON.

The Author gave the results of his experience, that the addition of carbonates of soda and potash prevent incrustations in boilers, as Kuhlmann and others had previously observed. He states that the addition of organic matters, such as rice-meal, was also found advantageous.

Detail of some Experiments on the Gases generated in a Sewer.

By MESSRS. MAURICE SCANLAN AND ALFRED ANDERSON.

The experiments by the authors were made upon the sewer in Friar Street, Southwark.

The sewer was in a very foul state, being 5 feet from the floor to the roof, and containing between 3 and 4 feet of deposit, which evolved a gas of a most powerful and filthy odour. To collect it, the authors used a circular funnel of tin-plate, which was inverted in the sewage matter of the sewer, and there kept floating at the surface by a board; to the top of this funnel was connected a gutta-percha delivering tube, from which the gas was obtained. The pressure of the gas was capable of overcoming that of 4 inches of water. The greatest amount collected in 24 hours amounted to 34 cubic inches, from an area of one square foot.

The chief circumstance of chemical interest connected with this subject, upon which very little has as yet been done, is the probable existence of the bisulphide of carbon in this sewer at the time of the experiments. Being, however, a very difficult substance to detect at any time, and more particularly when mixed with so many other compounds, the observations as to its positive existence are not to be considered as conclusive. At times its peculiar odour was strongly developed. Alcohol, through which the gas had passed, acquired a peculiar odour, resembling that of onions. In distilling this solution, results were obtained, confirming, to a certain extent, the existence of sulphide of carbon.

The mixture of gas was found to consist of sulphuretted hydrogen, carburetted hydrogen, carbonic acid and phosphuretted hydrogen; of the two latter a considerable proportion. A few minutes' exposure to the gas was sufficient to produce headache and nausea. The quantitative examination of the gases was not made.
