the scale. The unusally high value of the dielectric constant thus obtained is of interest.

The following results were obtained.

Table I.—Dielectric Constant of Selenium Oxychloride.

	At 20°.	At 10°.	Solid at 0°.
Cell 1	46.50	.....	.....
Cell 2	47.10	51.30	13.80
Cell 3	44.20	50.70	18.80

Liquid selenium oxychloride has a dielectric constant of 46.2 ± 1 at 20°, 51.00 ± 0.5 at 10° and a temperature coefficient of 1.04%.

Solid selenium oxychloride has a dielectric constant of 16.8 ± 2 at 0°.

This work was suggested by Dr. Herman Schlundt of the Department of Chemistry. His valuable assistance, in every way, is hereby acknowledged.

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VOLATILIZATION LOSSES OF PHOSPHORUS DURING EVAPORATIONS OF PHOSPHATES WITH SULFURIC ACID OR FUSIONS WITH PYROSULFATE.[1]

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I. Introduction.

Little has been written as to the possibility of volatilization losses of phosphoric acid during operations involving evaporation of phosphates with sulfuric acid or fusion with pyrosulfate, although these questions are of prime importance in the determination of phosphorus in rocks, ores, metallurgical products and many other materials. The experiments to be described were therefore undertaken with a view to determining whether any appreciable volatilization takes place, and in case of evidence of volatilization, to discovering contributing causes and preventive measures.

Rose[2] says in speaking of the treatment of phosphates with sulfuric acid, "Erhitzt man bis zum Verdampfen der Schwefelsäure so kann sich eine Spur Phosphorsäure verflüchtigen."

One of us[3] has repeatedly called attention to the fact that the possibility of loss of phosphorus pentoxide by volatilization during a pyrosulfate fusion or evaporation with sulfuric acid must be borne in mind.

Fresenius-Cohn[4] discuss losses of phosphorus pentoxide by volatiliza-

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[1] Published by permission of the Director of the Bureau of Standards.

[2] H. Rose, "Handbook of Quantitative Analysis," Finkener Ed., **2**, 575 (1871).

[3] W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks," U. S. Geol. Surv., *Bull.* **700**, p. 116; and earlier editions.

[4] Fresenius-Cohn, "Quantitative Chemical Analysis," J. Wiley and Sons, **1**, pp. 444–445 (1904).

tion as follows: "Bunce's[1] statement that phosphoric acid volatilizes when a phosphate is evaporated to dryness with hydrochloric or nitric acid and the residue heated a little, is quite erroneous. But, on the other hand, it must be borne in mind that orthophosphoric acid under these circumstances changes, not indeed at 100° C., but at a temperature still below 150°, to pyrophosphoric acid; thus, for instance, upon evaporating common hydrogen sodium phosphate with hydrochloric acid in excess, and drying the residue at 150°, we obtain $2NaCl + Na_2H_2P_2O_7$." Fresenius makes no mention of the behavior of a phosphate upon fuming with sulfuric acid or during a fusion with pyrosulfate.

II. Sources of Losses of Phosphorus Pentoxide.

A. Manipulation Losses.

Losses due to faulty manipulation are easily avoidable. Care must, of course, be taken during evaporation lest there be undue effervescence before the actual fuming of the sulfuric acid. Spattering during pyrosulfate fusions can be entirely avoided through the use of a properly prepared pyrosulfate,[2] a low initial flame, and only sufficient heat to keep the fusion molten.

B. Conversion Losses.

1. **Preliminary Remarks.**—Losses due to change of composition are occasioned by the conversion, under certain conditions of evaporation or fusion, of orthophosphoric acid into pyro- or metaphosphoric acids. These acids cannot be determined by any of the methods used for orthophosphoric acid, and hence failure to reconvert them into orthophosphoric acid may entail serious errors. The following reconversion procedures are quoted from Fresenius-Cohn:[3] "(1) In the dry way by protracted fusion with Na_2CO_3. This method is applicable only in case of alkali meta- and pyrophosphates, and of those metallic meta- or pyrophosphates which are completely decomposed by fusion with alkali carbonates; it fails with the salts of the alkaline earth metals, magnesium excepted. (2) In the wet way by heating with strong acid, best with concentrated sulfuric acid. This method leads to the attainment of only approximate results, in the case of all salts whose basic radicals form soluble salts of the acid added, because in these cases the meta- or pyrophosphoric acid is never completely liberated; but the desired result may be fully attained by the use of any acid which forms insoluble salt compounds with the basic radicals present. Respecting the partial conversion in the former case, I have found that it approaches the nearer to completeness the greater the quantity of free acid added, and that the ebullition must be long continued."

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[1] J. B. Bunce, *Am. J. Sci. Arts* [2] 11, 403–5 (1851).

[2] W. F. Hillebrand, *loc. cit.*, p. 116.

[3] Fresenius-Cohn, *ibid.*

TABLE I.—CONVERSION LOSSES.

Substance.	Treatment.	Precipitation conditions.	P_2O_5 calculated on basis of ignited phosphate obtained from. Converted aliquot. G.	Reconverted aliquot. G.	Error, G.	Reconversion Treatment.
H_3PO_4 (sp. gr. 1.88)	Heated for 2 hours at 240-265° in a platinum dish.	Double precipitation with magnesia mixture	0.1304	0.4990	—0.3686	Boiled with 10% H_2SO_4 for 2 hrs.
	Evaporated to cessation of fumes with 20 cc. of H_2SO_4 (sp. gr. 1.84)		0.1135	0.2449	—0.1314	
	Evaporated with 20 cc. H_2SO_4 (sp. gr. 1.84) for 2.75 hours, 10 cc. of H_2SO_4 evaporated		0.0713	0.0713	0.0000	
$NaNH_4HPO_4$	Evaporated to dryness with 4 successive 5 cc. portions of H_2SO_4 (sp. gr. 1.84)	Single precipitation	0.3192	0.3353	—0.0161	Fused with Na_2CO_3
	As above	Double precipitation	0.3148	0.3353	—0.0205	
	Evaporated to dryness with 2 cc. H_2SO_4 (sp. gr. 1.84)		0.0193	0.0291	—0.0098	
Na_2HPO_4	Evaporated for 3 hours with excess concentrated H_2SO_4 always present		0.1219	0.1222	—0.0003	Boiled with 10% H_2SO_4 for 2 hours
$4Al_2O_3.3P_2O_5$[a]	Evaporated to cessation of fumes with 12 cc. of H_2SO_4 (sp. gr. 1.84)	Precipitation as phosphomolybdate and then twice with magnesia mixture	0.0585[b]	0.0585	0.0000	Boiled with 10% H_2SO_4 and HNO_3 for 5 hours
$NaNH_4HPO$	Fused with 20 g. of $K_2S_2O_7$ at faint dull red for 2.25 hours	Double precipitation	0.0420	0.0638	—0.0218	
$4Al_2O_3.3P_2O_5$[a]	Fused with 10 g. of $K_2S_2O_7$ at a low temperature for 1.5 hours	Precipitation as phosphomolybdate and then twice with magnesia mixture	0.1285[b]	0.1286	—0.0001	
$6Fe_2O_3.P_2O_5$[a]	Fused with 5 g. of $K_2S_2O_7$ at a dull red for 2 hours		0.0067	0.0073	—0.0006	
$6Fe_2O_3.P_2O_5$[a]	Fused with 10 g. of $K_2S_2O_7$ at a dull red for 2 hours		0.0045	0.0054	—0.0009	

[a] Mixture artificially prepared.

[b] The classification "Unconverted" does not strictly apply here, since a certain amount of heating with acid was required to obtain perfect solution of the treated material.

2. **Experimental.**—In the experiments listed in Table I, phosphoric acid or phosphates were either evaporated with sulfuric acid or fused with pyrosulfate and then dissolved under conditions giving as little reconversion as possible. These solutions were then diluted to definite volume and aliquot portions taken for analysis with or without preliminary reconversion treatment. Double precipitations were usually carried out by first precipitating with magnesia mixture in excess, filtering without washing, dissolving the precipitate in a small amount of hydrochloric acid, reprecipitating in small volume after the addition of a few drops of magnesia mixture[1] and final washing with 10% by volume ammonium hydroxide solution. It was found that this procedure in addition to being more accurate than a single precipitation afforded a test for converted phosphates since these invariably caused a marked precipitation in the second filtrate and washings when excess magnesia mixture was added and the solution was allowed to stand for 12 hours. This precipitation is due to the fact that magnesium pyro- and metaphosphates are more soluble than the ortho-compounds. Consequently if pyro- or meta- compounds are present the addition of an excess of magnesia mixture in the first precipitation results in a more complete deposition than takes place in the second precipitation where the precipitant is present in very slight excess. In addition to this, the thorough washing of the second precipitate with 10% (by volume) ammonium hydroxide results in a partial solution of the pyro- and meta- compounds which are then again precipitated in the filtrate upon standing. The data in Table I demonstrate that: (1) orthophosphoric acid and secondary (presumably also primary) phosphates suffer marked conversion upon evaporation to dryness with sulfuric acid, and serious errors will ensue in these cases if phosphate determinations are subsequently carried out without reconversion treatment; (2) no conversion need be feared in evaporations involving the continuous presence of excess sulfuric acid; (3) secondary (and presumably also primary) orthophosphates suffer partial conversion during fusions with pyrosulfate and require reconversion treatment before precipitation by ordinary methods. Basic orthophosphates may suffer conversion.

In the light of the experiments performed, it is apparent that all phosphate-bearing residues obtained through evaporation with sulfuric acid to cessation of fumes, and all pyrosulfate fusions of phosphate material should be boiled with acid, preferably 10% sulfuric acid, for at least 2 hours before precipitation as phosphomolybdate or magnesium ammonium phosphate.

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[1] F. A. Gooch and M. Austin, *Am. J. Sci.*, [4] 7, 187–198 (1899), state that the first phosphate precipitate should be filtered off, dissolved in hydrochloric acid and reprecipitated by ammonia without further addition of magnesia mixture. This statement, which has been copied in several texts, is wrong, since this procedure is sure to lead to an incomplete final precipitation.

C. Volatilization Losses.

1. Upon Evaporation with Sulfuric Acid.—Since phosphorus compounds begin to volatilize from phosphoric acid at temperatures near 270°, losses are to be expected when sulfuric acid solutions of phosphates are evaporated at temperatures near this point. Sulfuric acid may, however, be volatilized at temperatures much lower than this and therefore the experiments listed in Table II were carried out to ascertain the extent of the losses which might be expected when phosphate solutions were evaporated at low temperatures (just fuming) with excess of conc. sulfuric acid, as compared with the losses experienced in evaporations carried on at higher temperatures and to the partial or complete expulsion of all sulfuric acid. Solutions of phosphoric acid, secondary phosphates and basic phosphates were accordingly evaporated with sulfuric acid under conditions specified in Table II, in platinum dishes placed in a "radiator."[1] The solutions or residues were then subjected to reconversion treatments and analyzed for their phosphorus pentoxide content.

TABLE II.—EVAPORATION OF SULFURIC ACID SOLUTIONS OF PHOSPHATES.

Compound taken.	H_2SO_4. Cc.	Treatment Temp. ° C.	Treatment Time. hrs.	H_2SO_4 volatilized. Cc.	P_2O_5 taken. G.	P_2O_5 found. G.	Error. G.
H_3PO_4	20	135–145	2.25	7	0.0714	0.0714	0.0000
	20	145–155	2.75	10	0.0714	0.0713	—0.0001
	20	200+	4.00	20	0.0714	0.0612	—0.0102
$NaNH_4HPO_4$	20 in 4–5 cc. portions	.....	5.75	20	0.3510	0.3399	—0.0111
	20	.....	5.75	20	0.3510	0.3475	—0.0035
Na_2HPO_4	20	low gradual fuming	3	5	0.0043	0.0041	—0.0002
$4Al_2O_3.3P_2O_5$[a]	12	150	1.5	3	0.1366	0.1366	0.0000
	12	165	3	5	0.1366	0.1348	—0.0018
	12	165+	3	12	0.1366	0.1170	—0.0196
	20	150	3	3	0.0057	0.0057	0.0000
$4Al_2O_3.3P_2O_5$	5 drops of H_2O, 5 drops of 1 : 1 H_2SO_4, 5 cc. of HF, volatilized at lowest possible temp. in a platinum crucible, then ignited, and finally dissolved.[b]				0.0057	0.0057	0.0000
Na_2HPO_4					0.0045	0.0045	0.0000

[a] See Table I.

[b] To imitate the conditions obtaining when an impure silica containing phosphates, such as titanium or zirconium phosphates, is treated with HF and H_2SO_4.

The data in Table II demonstrate that: (1) volatilization losses of phosphorus pentoxide will surely ensue when phosphoric acid or phosphates are evaporated with sulfuric acid to complete expulsion of fumes; (2)

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[1] W. F. Hillebrand, *loc. cit.*, p. 33.

losses will occur if evaporation takes place at elevated temperatures even though sulfuric acid is continuously present in excess; (3) slight losses may occur upon prolonged evaporation with conc. sulfuric acid at temperatures near 150°; (4) no losses need be feared when solutions of phosphates are slowly evaporated with sulfuric acid (preferably in a radiator and not over a free flame) to the first appearance of fumes; (5) no losses need be feared in a hydrofluoric-sulfuric acid treatment of a silica contaminated by phosphorus pentoxide, provided a slight excess only of sulfuric acid is used and the evaporation is carried on slowly in a radiator. Losses will occur if excessive amounts of sulfuric acid are used. That the losses listed were true volatilization losses and not losses due to failure in reconversion, was definitely established by qualitative and quantitative tests which showed the presence of phosphorus pentoxide in the vapors given off during the evaporations which resulted in low phosphorus pentoxide values.

The experiments listed in Table II were carried out by the junior author. Many years ago, and again more recently, the senior author obtained losses, when treating sodium phosphate, that were much greater than any of those above reported. Presumably the volatilization was much more forced than in the present series of tests.

2. Upon Fusion with Pyrosulfate.—The question as to volatilization losses during pyrosulfate fusions is important, since many precipitates obtained by ammonium hydroxide in rock analyses carry phosphorus pentoxide and it is often desirable to determine the amount after fusion with pyrosulfate. The experiments listed in Table III were carried out in covered platinum crucibles at temperatures ranging from the very dull red of ordinary fusions, to the higher temperatures which analysts sometimes vainly employ in an attempt to "force" a fusion. The cooled fusions were dissolved, treated to effect reconversion and then finally precipitated twice with magnesia mixture. The experiments in Table III indicate that: (1) pyrosulfate fusions of secondary phosphates result in decided losses of phosphorus pentoxide by volatilization; (2) fusions of basic phosphates (comparable with most of the fusions carried on in most

TABLE III.—FUSION OF PHOSPHATES WITH PYROSULFATE.

The heating was to dull redness in all experiments.

Compound used.	$K_2S_2O_7$ taken. G.	Duration of fusion. hrs.	P_2O_5 taken. G.	P_2O_5 found. G.	Error. G.
$NaNH_4HPO_4$	10	2.5	0.0700	0.0680	−0.0020
	20	2.25	0.0700	0.0638	−0.0062
	5	2	0.0045	0.0039	−0.0006
$4Al_2O_3.3P_2O_5$[a]	5	1	0.1749	0.1748	−0.0001
	5	2	0.0057	0.0057	0.0000
$6Fe_2O_3.P_2O_5$[a]	10	2	0.0055	0.0054	−0.0001
	5	2	0.0078	0.0075	−0.0003

[a] See Table I.

analyses) in covered platinum crucibles at low temperatures, do not ordinarily occasion serious losses. Since losses may occur in such fusions, they should be avoided when accurate determinations of phosphorus pentoxide are desired.

Qualitative and quantitative tests of the vapors given off during special fusions in Gooch tubulated crucibles demonstrated that the phosphorus pentoxide losses were true volatilization losses and were not due to incomplete reconversion treatments.

III. Summary.

1. No volatilization losses of phosphorus occur during evaporations of sulfuric acid solutions of phosphates, provided the evaporations are carried on at temperatures below 150° and stopped when fumes appear. Such evaporations are best performed over "radiators."

2. Volatilization losses during evaporation of sulfuric acid solutions of phosphates are occasioned by (1) evaporation to complete expulsion of sulfuric acid; (2) evaporation at high temperatures such as 200–260°; and (3) unduly prolonged evaporation at temperatures above 150°. Evaporations involving only a drop or two of sulfuric acid, such as apply in silica treatments, do not cause measurable losses.

3. Fusions with pyrosulfate in *covered* crucibles and at dull red temperatures result in appreciable losses in the case of secondary (and presumably primary) phosphates, and may result in slight losses in the case of basic phosphates.

4. Orthophosphoric acid and primary and secondary orthophosphates suffer conversion to pyro- and metaphosphoric acid or phosphates when evaporated to dryness with sulfuric acid or fused with pyrosulfate; such "converted" compounds must be subjected to "reconversion" treatments before precipitation with molybdic acid or magnesia mixture.

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NOTE.

Correction.—In the articles "Adsorption by Charcoal," I and II, appearing in the July number of THIS JOURNAL, mention of the fact that the work was made possible by a grant from the "Elizabeth Thompson Science Fund" was overlooked. We would like at this time to express our thanks publicly for that assistance.

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