

## ON THE ANALYTICAL PROPERTIES OF IRON PHOSPHIDE AND PHOSPHATE.

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I N the year 1886, Cheever, in an article in the *Transactions of the American Institute of Mining Engineers*, **15**, 448, sought to explain the variation in effect of a definite amount of phosphorus upon the properties of iron and steel by assuming that the phosphorus exists in the metal in two conditions; *viz.*, as phosphide, which is harmful, and as phosphate, which is harmless, or comparatively so. To demonstrate this he used the following method:

"A weighed sample of iron is treated in the cold with a solution of the double chloride of copper and ammonium until the iron is all dissolved, then filtered without washing. The residue of copper, carbon, phosphorus, etc., is next digested at 50° C. for two hours with 100 cc. of a saturated solution of ammonium oxalate, then filtered and washed; the filtrate contains the phosphate of iron; the residue the phosphide."

Later, in the same article, he shortens the method as follows:

"The copper, carbon, phosphorus, etc., residue is shaken in a flask for five minutes with seventy-five cc. of a cold, one per cent. solution of hydrochloric acid (two cc. strong hydrochloric acid to 100 cc. water—free from chlorine), then filtered and washed with water, the filtrate made strongly acid with nitric acid and evaporated nearly to dryness, and the phosphorus precipitated by molybdate solution."

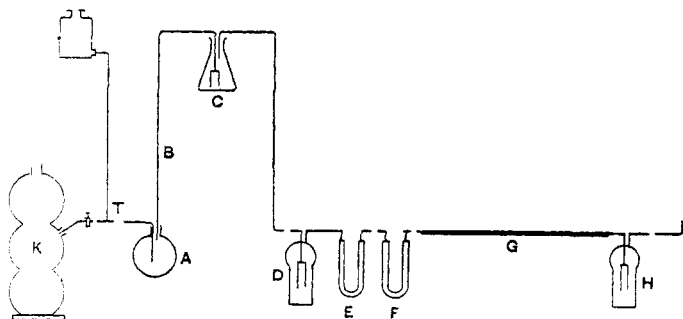
In a second paper in the same Journal, **16**, 269, Cheever gives results obtained by another method, he here volatilizing the iron as chloride by chlorine, "and analyzing the residue for phosphorus, which, if present, must be in the form of phosphoric acid; for the iron phosphide would be volatilized."

At that time doubt was cast upon the accuracy of Cheever's work because of the uncertainty as to the behavior of phosphide of iron towards the different reagents which he employed. In the hope of removing some of that uncertainty the authors entered upon the experimental work detailed below.

Preliminary work upon the phosphides of iron carried out by Mr. Russell Elliott in this laboratory in 1891-2, seemed to show that the different phosphides, of which, according to Freese,<sup>1</sup> there are three,  $\text{Fe}_3\text{P}$ ,  $\text{FeP}$ , and  $\text{Fe}_2\text{P}$ , behave quite similarly towards various solvents. For this reason, and also because of the length of time required for the preparation of a pure sample, we prepared and examined only one of the phosphides, selecting that which is formed by treating anhydrous ferrous chloride with phosphine at a red heat.

*Ferrous Chloride.*—The purest piano wire obtainable was placed in a combustion tube, which was connected on one side with an apparatus furnishing dry hydrochloric acid gas, and on the other side with a Schiff nitrometer<sup>2</sup> filled with strong potassium hydroxide solution. When the air in the tube had been completely displaced by the hydrochloric acid gas, as was shown by the complete absorption of the gas by the caustic potash solution, the combustion tube was heated to redness. The ferrous chloride produced was partly in the form of glistening light-yellow plates, and partly a yellowish amorphous powder. Careful tests showed that it was completely free from ferric chloride.

*Phosphine.*—The phosphine was generated by the action of a solution of potassium hydroxide upon phosphorus. The form of apparatus finally adopted has given such satisfactory results that a brief description of it may not be out of place. It consists of:



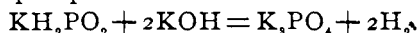
1. The 500 cc. distilling flask A in which the phosphine is generated.

<sup>1</sup> *Pogg. Ann.*, 132, 225.

<sup>2</sup> *Ztschr. anal. Chem.*, 7, 430.

2. The upright tube B which serves as a condenser, and which is widened after entering the cooling flask C to prevent its becoming clogged by the condensation of the phosphorus.
3. The cooling flask C which is surrounded with ice-water.
4. The wash-bottle D.
5. The two U tubes, E and F, filled with calcium chloride for drying the gas.
6. The combustion tube G.
7. The wash-bottle H which prevents the air from diffusing back into the combustion tube.
8. A Kipp apparatus, K, for generating hydrogen.
9. The J tube T, through which water could be driven into A from the reservoir above in order to stop the generation of the phosphine by diluting the caustic potash solution.

The most uniform evolution of phosphine was obtained by using a 1 : 1 solution of potassium hydroxide, a stronger solution causing a more rapid generation of the gas than was desirable. Although the phosphine resulting from the use of this moderately concentrated caustic potash was not as pure as that obtained with a very concentrated solution,<sup>1</sup> yet the phosphide obtained was probably not influenced to any great extent by the small amounts of hydrogen given off early in the phosphine evolution. The hydrogen would reduce some of the ferrous chloride to metallic iron, but if we accept the statement of Freese,<sup>2</sup> the product is the same whether phosphine acts upon anhydrous ferrous chloride or upon metallic iron. To avoid, however, the production of any unnecessarily large amount of hydrogen the contents of the generating flask was at no time heated to boiling, this precaution serving to lessen the amount of hydrogen arising from the secondary reaction between the potassium hydroxide and potassium hypophosphite :



It was thought that the hydrogen thus set free might reduce the phosphide after the latter had formed, but later experiments with the pure phosphide showed that it was not reduced when highly heated in a current of hydrogen. The solution of potassium hydroxide should be cooled before being poured upon the

<sup>1</sup> A. W. Hofmann, *Ber. d. Chem. Ges.*, 1871, 200.

<sup>2</sup> *Pogg. Ann.*, 132, 225.

phosphorus in the flask, in order to avoid the immediate generation of any phosphine, as that would cause an explosion upon coming in contact with the air in the flask. As soon as all connections had been made, hydrogen from the Kipp generator was run through the apparatus until all air had been expelled. The sand-bath under the generating flask was then gently heated until the phosphine began to come off somewhat rapidly. The hydrogen was then shut off and the flame removed, the latter being replaced only when the solution of the gas had nearly ceased. This procedure greatly lengthened the duration of the current of phosphine.

When nearly all of the hydrogen had been driven from the apparatus the phosphine burst into flame at the end of the outlet tube. The combustion tube was then heated. As soon as the hydrochloric acid gas, formed by the action of the phosphine upon the ferrous chloride, began to come off, the flame at the outlet tube ceased to burn. The ferrous chloride gradually darkened, and after half an hour, when the reaction was completed, it had assumed a dark bluish-gray color.

Upon breaking the tube there was found a brittle, porous substance which rarely showed any crystalline structure. It was powdered in an agate mortar, then digested with hot hydrochloric acid (1 : 12) until it was not at all attracted by the magnet, and was finally dried over sulphuric acid in an atmosphere of carbon dioxide.

*Analysis of the Phosphide.*—Stöckmann<sup>1</sup> states that he always obtained too low results for phosphorus when aqua regia was used as a solvent for spiegeleisen. He also tested the gases which were given off when the sample was dissolved, by passing them through an oxidizing medium, and in each case was able to detect phosphorus in them. For this reason we first tried other solvents, but although the phosphide was quite strongly attacked by nitric acid and by hydrochloric acid, and especially by nitric acid to which potassium chlorate was gradually added in small amounts, complete solution was in no case effected even by several hours treatment.

Portions of the phosphide were then treated with aqua regia in a small flask to which a return-flow condenser was attached.

<sup>1</sup> *Ztschr. anal. Chem.*, 16, 175.

After passing through the condenser the escaping gases were passed through a Mitscherlich bulb containing a solution of potassium hydroxide which had previously been saturated by chlorine. After the phosphide had been completely dissolved, the potassium hydroxide solution was acidified with nitric acid and was repeatedly evaporated with nitric acid until all chlorine had been expelled. Ammonium molybdate was then added, but no trace of a precipitate resulted. Aqua regia was, therefore, adopted as the solvent for the phosphide.

The following method of analysis was first tried :

About 0.1 gram of the phosphide was dissolved in aqua regia (one part of nitric acid to three parts of hydrochloric acid), and the solution, after being diluted, was precipitated by ammonium hydroxide. An excess of ammonium sulphide was then added to break down the ferric phosphate, and the solution was kept at 70° C. for fifteen hours. The ferrous sulphide was then filtered off, dissolved in dilute hydrochloric acid, and the iron then oxidized by bromine water. Upon precipitating this solution with ammonium hydroxide and weighing the iron as ferric oxide, too high results were obtained since the precipitate was found to contain phosphoric acid.

The method finally adopted for the analysis of the phosphide was as follows :

The sample was dissolved in aqua regia, the solution repeatedly evaporated with nitric acid, and the phosphoric acid determined by the molybdate-magnesia method. To determine the iron in the filtrate from the ammonium phosphomolybdate precipitate, the method of W. H. Krug<sup>1</sup> was used with satisfactory results. The iron was precipitated in the cold with ammonium hydroxide, and the ferric hydroxide, after thorough washing, was dissolved in nitric acid and again precipitated from the cold solution with ammonium hydroxide. After washing until all chlorides had been removed, the iron was weighed as Fe<sub>2</sub>O<sub>3</sub>.

The results obtained were as follows :

	Found.	Calculated for	
		Fe <sub>3</sub> P <sub>4</sub>	FeP
Fe .....	64.21	57.52	64.36
P .....	35.62	42.48	35.64

<sup>1</sup>J. Anal. Appl. Chem., 5, 674.

The work of other investigators in this field had led us to expect as a product, not FeP but  $\text{Fe}_3\text{P}_4$ . Yet the constancy of composition shown by separately prepared portions of our product, its completely non-magnetic character and the agreement of the analysis with the calculated percentages, leave but little doubt as to the purity and identity of the phosphide.

The fact that the true phosphides of iron are *non-magnetic* seems to have been overlooked by recent writers, a circumstance which has probably led Hvoslef, Schneider, Percy, and others, to regard a mixture of phosphide of iron and iron (they give it the formula  $\text{Fe}_3\text{P}$ ) as a definite phosphide. Howe<sup>1</sup> cites the work of Hvoslef and Percy, and says: "These facts suggest that iron and phosphorus preferentially combine in this particular ratio." But he does not mention the careful and extended researches of Freese upon this subject, who says:<sup>2</sup> "Endlich habe ich versucht, das von Hvoslef beschriebene Phosphoreisen  $\text{Fe}_3\text{P}$ , welches derselbe durch Glühen des Phosphorets FeP unter einer Decke von Borax erhalten haben will, darzustellen, allein bis jetzt vergeblich." After describing some of his own experiments, made according to Hvoslef's method, Freese concludes: "Hieraus schliesse ich, dass Hvoslef's Phosphoreisen nur ein Gemenge von Eisen mit Phosphoreisen ist, denn stets fand ich bei einem anerkannt reinen Eisenphosphoret den nach längerer Behandlung mit heisser Chlorwasserstoff säure verbliebenen Rückstand mit dem Phosphoret gleich zusammengesetzt."

*Ferric Pyrophosphate.*—This salt was chosen as representing perhaps more nearly than any other the condition of the oxidized phosphorus in iron and steel. A sample of the pure ferric pyrophosphate was heated for half an hour over the full Bunsen flame: it retained its yellow color and was completely soluble in concentrated hydrochloric acid.

*Experiments with Solvents.*—Before attempting to separate the phosphide of iron from the pyrophosphate in samples of iron or steel, it was necessary to find a solvent which would completely dissolve the pyrophosphate and leave the phosphide unattacked. The reagents tried were solutions of ammonium oxalate, potassium oxalate, ammonium citrate, ammonium carbonate, ammo-

<sup>1</sup> Metallurgy of Steel, p. 55.

<sup>2</sup> Pogg. Ann., 132, 262.

nium cupric chloride, and dilute solutions of chromic, sulphuric, nitric, and hydrochloric acids; both rapid boiling and long digestion at 100° C. were employed. Clear solutions of the pyrophosphate were obtained only with ammonium oxalate, ammonium citrate, and hydrochloric acid. Portions of fifty milligrams of the pyrophosphate were then digested on a hot plate with 100 cc. of each of these three solvents. Complete solution resulted

with hydrochloric acid (1:1).....	in 2 minutes
“ ammonium oxalate (concentrated)..	“ 45 “
“ “ citrate (sp. gr. 1.09) ....	“ 90 “

On diluting the ammonium oxalate solution with water a white precipitate resulted, and as this could be dissolved only by adding hydrochloric acid and boiling, the use of ammonium oxalate was abandoned.

One hundred milligram portions of the phosphide were then treated with hydrochloric acid and ammonium citrate under the same conditions as were required for the complete solution of the pyrophosphate. The residues were collected on counterpoised filters, dried, and weighed. It was found that the phosphide which had been digested with hydrochloric acid had lost about four per cent. of its weight. The filtrate from this portion, after the hydrochloric acid had been expelled by evaporation with nitric acid, gave strong tests for both iron and phosphorus. The sample of phosphide which had been digested with ammonium citrate showed no appreciable loss of weight, and hence a solution of this reagent, of a sp. gr. of 1.09, was used in the following experiments upon the separation of the pyrophosphate of iron, and phosphide of iron, in samples of iron and steel.

Before trying the ammonium citrate solution a preliminary experiment was made to ascertain the nature of the action of hydrochloric acid (1:1) upon the phosphorus in iron. A sample of pig iron, containing 0.205 per cent. total phosphorus, was treated with the acid until all action had ceased. The solution was filtered, the filtrate evaporated with nitric acid, and the phosphorus determined by the molybdate-magnesia method. Two determinations gave 0.153 and 0.154 per cent. phosphorus. The determination of the phosphorus in the unattacked residue showed that only 0.008 per cent. remained behind, from which

it follows that over twenty per cent. of the phosphorus present escaped in gaseous form during the solution of the iron.

The ammonium citrate separation was then tried on two samples of steel to ascertain whether the method would give agreeing results. The sample should be as finely divided as possible, and for this reason filings were used in the following determinations:

Five grains of "Open Hearth" steel was digested on a hot plate ( $100^{\circ}$ ), with ammonium citrate solution, for an hour and a half. The solution was then filtered through asbestos. The residue was thoroughly washed with water, dissolved in nitric acid (1.20 sp. gr.), and the phosphorus determined by the molybdate-magnesia method.

Total phosphorus in the sample was 0.044 per cent.

Phosphorus in the residue after treatment with ammonium citrate, 0.033 and 0.032 per cent.

A sample of Bessemer steel, containing 0.107 per cent. total phosphorus, gave by the same method 0.046 and 0.053 per cent. of phosphorus in the residue.

No further analyses of iron or steel samples were made, for our object in taking up the work was not the investigation of the condition of phosphorus in samples of commercial products, but was merely to attempt to devise a method to separate phosphide of iron from pyrophosphate.

The chlorine method employed by Cheever was also tried on the phosphide and pyrophosphate.

Eighty milligrams of the phosphide were heated in a current of dry chlorine. As the temperature rose sparks shot out from the surface of the phosphide. At a low red heat a glow ran through the substance which then melted and volatilized completely in a few minutes.

A sample of the ferric pyrophosphate was then heated for half an hour in a current of chlorine at the highest temperature obtainable by the use of a combustion furnace, but no loss in weight resulted.

A mixture of 0.0435 gram of the pyrophosphate, with 0.0292 gram of the phosphide, was then heated in chlorine in the same manner. The residue in the boat weighed only 0.0231 gram. As this seemed to indicate that in the volatilization the phos-



phide exerts some reducing action on the pyrophosphate, causing a volatilization of some of the constituents of the latter compound, another experiment was tried with a mixture containing a slightly higher per cent. of phosphide, to see whether there would be a correspondingly greater loss in the pyrophosphate.

0.0561 gram of the pyrophosphate, and 0.0472 gram of the phosphide, treated with chlorine, gave a residue weighing 0.0193 gram, a result which seems to sustain the above supposition.

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### NOTES ON ALUMINUM.<sup>1</sup>

BY GEORGE FREDERICK ANDREWS.

THE writer of this paper has made a large number of experiments with aluminum particularly with reference to its use in jewelry etc. The facts stated are the results of some of these experiments.

*Alloys containing Gold.*—The alloys of gold and aluminum are interesting, though of little practical use except for decorative purposes. The alloy with six per cent. of gold is as white as pure aluminum but much more brittle. The alloy with ten per cent. of gold is harder than aluminum but does not work well, except at a high temperature. Its color is light violet-brown. The alloy with fifteen per cent. of gold is a very soft fine-grained metal. It has a slight violet tint, although nearly white. The alloy with fifty per cent. of gold has a beautiful violet color. It is very soft and spongy. The alloy with seventy-eight per cent. of gold is very brittle. The color is peculiar; it is between pink and violet. The alloy with ninety per cent. of gold has a pale violet color, while the alloy with ninety-four per cent. of gold has a color approaching pink again. Alloys containing small percentages of aluminum leave a bright violet color on the cupel, under the blowpipe.

An alloy containing fifty per cent. of gold, forty-five per cent. of copper, and five per cent. of aluminum takes the color and polish of fourteen carat gold but easily tarnishes. This alloy has also been used in electroplating, but it is not entirely satisfactory for this purpose.

*Alloys containing Silver.*—Alloys containing from four to eight

<sup>1</sup> Abstract from a paper read before the Rhode Island Section, February 15, 1894.