RESULTS

The results obtained are given in the accompanying set of tables and plots. Before making the plots, two preliminary sets were made, one using relative and the other absolute humidities. It was found that the results could be plotted against the relative humidity only, except in the case of the penetration tests, where the results yielded a curve only when plotted against the absolute humidity.

It will be noted that the results here given agree with those obtained by Kress and Silverstein in the case of the Mullen test plot only. These variations may have been due to the higher grades of paper used in our tests, but this seems rather doubtful, as no such variations were observed over the range of qualities tested here.

It was found impossible to draw a curve for "penetration" for sample "H" owing to the wide variations noted between different tests at the same humidity. In the "folding-cross" tests no curve could be drawn for "C," the points being as shown on the drawing. The "folding-machine" tests for B and C were so far beyond the range of the other samples that their curves are presented on a different scale.

SUMMARY

The magnitude of most of the tests decreased 40 to 50 per cent as the relative humidity increased from 50 to 98 per cent. The stretch in the machine direction increased about 30 per cent and in the cross direction about 40 to 50 per cent under the same circumstances.

The results of the folding tests in the machine direction tended to reach a maximum at about 80 per cent relative humidity in all except two cases. In the cases of samples "B" and "C," the curve plotted from the results of this test increased very rapidly with the increase of relative humidity and tended to become asymptotic to about the 95 per cent humidity line.

The time of ink penetration decreased 40 to 50 per cent as the absolute humidity increased from 6 grains per cubic foot of air (55 per cent relative humidity at 80° F.) to 11 grains per cubic foot (100 per cent relative humidity at 80° F.).

Special attention is called to curves "B" and "K." These samples were the same in every way except that "B" was tub sized and "K" was not. The advantages of a good tub size are very clearly shown.

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THE OCCURRENCE OF GERMANIUM IN MISSOURI AND WISCONSIN BLENDES¹

By G. H. BUCHANAN

Of the fifty or more elements which we usually distinguish as rare, few are more worthy of the distinction than the element germanium. Discovered in 1886 by Winkler in a new silver mineral, argyrodite, and identified by him as the eka-silicon of Mendeléef, it has dropped back into oblivion since the days of

this classic work, until to-day it is one of our least known elements. With but few exceptions our entire knowledge of the properties of the element is due to Winkler. According to Urbain,¹ the material worked over by Winkler for the preparation of germanium was a mixture of argyrodite with other minerals, and did not contain more than 0.36 per cent of argyrodite. Since the germanium content of argyrodite is 6 to 7 per cent, the germanium content of his raw material could only have been between 0.02 and 0.03 per cent. From this material Winkler obtained 80 kilos of mixed metallic sulfides which yielded 156 g. pure germanium.

Argyrodite, the richest source of the element heretofore known, has proved exceedingly rare, and during the thirty years that have elapsed since the work of Winkler only a very few additional sources of the element have been brought to light.

Krüss has reported the presence of 0.1 per cent germanium in euxenite. Its occurrence in samarskite, tantalite and niobite has been reported and denied, a disagreement which is not surprising in view of the complexity of these minerals. Two other sources have been more recently discussed. Urbain² by spectroscopic methods detected germanium in 38 out of 64 blendes from various localities. Taking 550 kilos of one of these, a Mexican blende, he obtained from it 5 g. pure germanium. Bardet,³ also by spectroscopic methods, detected traces of germanium in certain French mineral waters. Since the recovery of germanium from blendes by the method of Urbain was long and costly, he believed that the residues from these mineral waters might yield sufficient germanium to provide for the needs of scientific study. From 100 kilos of residues, representing 250,000 liters of mineral water, he obtained 60 mg. GeO₂.

A more recent report of the occurrence of germanium is due to W. F. Hillebrand and J. A. Scherrer:⁴ in a paper on "The Recovery of Gallium from Spelter in the United States," mention is made of an examination for germanium of a number of blendes, carried on at the Bureau of Standards by Dr. K. Burns. By the use of the spectroscope germanium was identified in several of these, notably in a Missouri sulfide. A short paper by the writer was published in *THIS JOURNAL* in July, 1916, p. 585, relating to the identification of germanium in zinc-bearing materials. At that time it was not possible to give details as to the origin of the rich germanium-bearing material. It is the purpose of the present paper to discuss the nature of this material, which now appears to be the richest source of the element known.

During the summer of 1915 there was brought to the writer's attention an oxide of zinc which had been prepared from spelter residues by the American process. A chemical examination revealed the presence of considerable quantities of an unusual constituent, which was identified as the element germanium.

The identification tests consisted in a distillation of

¹ *Compt. rend.*, **150**, 1758.

² *Ibid.*, **149**, 602.

³ *Ibid.*, **158**, 1278.

⁴ *THIS JOURNAL*, **8** (1916), 225.

¹ Presented at the *Symposium on the Chemistry and Metallurgy of Zinc*, 54th Meeting American Chemical Society, Kansas City, April 10 to 14, 1917.

the oxide of zinc with hydrochloric acid, a slow current of chlorine being bubbled through the solution during boiling to prevent distillation of arsenic. The strongly acid distillate was diluted and saturated with hydrogen sulfide. A voluminous white precipitate was formed which was readily soluble in alkalies and which dissolved in water, although more slowly. The sulfide was slowly re-precipitated from its aqueous solution upon addition of strong acids. The addition of hydrofluoric acid to the aqueous solution of the sulfide, followed by saturating the mixture with solid potassium chloride, produced a grayish, gelatinous precipitate, the double fluoride of potassium and germanium.

A roughly quantitative determination of the ratio $\text{GeO}_2 : \text{GeS}_2$ gave the value 0.747. The theoretical ratio, assuming 72.5 for the atomic weight of germanium, is 0.766. The sulfide precipitate was weighed without washing free from precipitated sulfur, since the usual alcohol-carbon bisulfide washing caused the precipitate to run through the asbestos Gooch. The presence of sulfur in the precipitate when weighed would, of course, lower the ratio. Bearing this in mind, the agreement between calculated and observed values is fairly close.

By distilling weighed samples of the oxide of zinc with chlorine and hydrochloric acid, and precipitating and weighing the sulfide, the value $\text{GeO}_2 = 0.25$ per cent was obtained.

A sample of the oxide of the element, prepared by ignition of the sulfide and treatment of the residue with nitric acid, was examined at the Bureau of Standards with the spectroscope and was reported, "Germanium, principal constituent."

As has been stated, the oxide of zinc in which this considerable amount of germanium was detected was prepared from spelter residues. The attempt was now made to locate geographically the source of the element.

The residues in question were mixed residues from Joplin and Wisconsin ores. An examination of a number of oxides of zinc prepared from ores from various localities, including those made from Missouri and Wisconsin ores, was now undertaken. For this work a delicate test for the presence of germanium was required. The following procedure was applied with success to a large number of samples; the details are those which were found necessary with this class of material. The essential details of the method are due to A. A. Noyes:

Weigh a 100-g. sample of the oxide of zinc into a liter distilling flask connected with a water-cooled condenser, and add 200 cc. concentrated hydrochloric acid. Pass chlorine into the mixture until the gas appears in the receiver of the condenser, and then heat the mixture to boiling and distil to about half volume, continuing the passage of a slow current of chlorine. Dilute the distillate with an equal volume of water and pass hydrogen sulfide into it for at least 30 minutes. If no precipitate is formed (other than the usual opalescence due to sulfur), germanium is absent. If

a precipitate is formed, filter it off on a small paper and wash it with a very little cold water.

Place the paper containing the precipitate in a flask with about 150 cc. water, boil for 15 minutes, and filter. To the filtrate add 50 cc. concentrated hydrochloric acid, cool and treat with hydrogen sulfide as before. A white flocculent precipitate indicates the possible presence of germanium.

Filter on a small paper and wash once with a little cold water. Pour ammonia through the filter, receiving the solution and washings in a platinum dish. Evaporate to dryness. Moisten the residue with concentrated nitric acid and evaporate to dryness again. When dry, ignite for a few minutes.

To the residue add a very little water and a few drops of hydrofluoric acid, saturate with solid potassium chloride and allow to stand in the cold for 15 minutes. If germanium is present a grayish, gelatinous precipitate is formed, soluble on heating or diluting the solution.

The presence of germanium is not reported unless this last confirmation test is obtained.

With this procedure positive results were obtained with both Joplin and Wisconsin Separator ores. Positive results were also obtained from Mineral Point "Special Leaded Oxide of Zinc," from an oxide made from a Mexican ore (La Bufa), and from one or two others. Negative results were had from two other Mexican ores, from ore from Austinville, Va., from Mineral Point "Prime Oxide of Zinc," and from New Jersey ores ("XX Oxides"). In all cases where positive results were obtained the amounts detected were very much less than were met with in the oxide made from spelter residues, probably not one-tenth as much. It is probable that the procedure described would detect as little as 0.01 per cent germanium in an oxide of zinc.

It is evident from these results that the germanium content of the residuum may have been derived from either the Wisconsin or the Missouri ore, or from both of them, and that it has been greatly concentrated during the metallurgical treatments which it has undergone. The treatment in the spelter retorts and in the oxide fires has carried on this concentration on an enormous scale and we have, as a result, an abundance of a material much richer in germanium than the original ores.

The properties of the substance as given in the literature explain the nature of this concentration. The metal is said to be readily obtained by reduction of the oxide with carbon at a red heat, so that under the conditions prevailing in the spelter retort the germanium must be present in the elementary state. It is not markedly volatile at 1350°C . Accordingly, while the zinc was distilling off into the condenser, the germanium *for the most part* remained behind, and was discharged with the residues. The qualification seems necessary, since Uhler has detected traces of germanium in the leady residues from the redistillation of low-grade metal.¹ In the zinc oxide furnaces the ger-

¹ Browning, "Introduction to the Rarer Elements," 4th edition, p. 84.

manium burned to oxide and passed off with the zinc smoke into the bags.

It is possible to obtain a rough approximation of the amount of germanium in the original ore by assuming a zinc oxide content of 10 per cent for the residues, and of 50 per cent for the original ore. Assuming in all cases complete recoveries, the GeO_2 content of the residues would have been one-tenth that of the oxide of zinc, or 0.025 per cent, and that of the original ore would have been approximately 0.01 per cent.

The work reported in the preceding paragraphs was carried on by the writer in the Research Laboratory of The New Jersey Zinc Company, at Palmerton, Pennsylvania, to the officials of which company the writer is under obligations for permission to publish these results. Through the kind offices of Mr. George C. Stone, of the New Jersey Zinc Company, a supply of the germaniferous oxide of zinc has been furnished the Massachusetts Institute of Technology for study. This work has already been begun.

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PHOSPHOR-TIN AND A VOLUMETRIC METHOD FOR ITS ANALYSIS

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The paper presented here traces its origin to a request forwarded to this laboratory for a method for the rapid and accurate analysis of an alloy of phosphorus and tin, known commercially as "phosphor-tin." This material is purchased according to specifications. Analysis of each shipment, therefore, is desirable. Furthermore, since the correct proportions of the material to be used in the various processes can be determined only from a knowledge of its composition such an analysis is practically necessary. It is obvious, therefore, that a method corresponding to the description in the request should be available. No such method, however, was found in the literature.

In this connection it may be contended that inasmuch as the tin in the alloy can be readily determined by some standard method, such as the sulfide method, and the percentage of phosphorus estimated by the "method of difference," that the problem presented was not one difficult of solution. It should be noted, however, that the presence of any impurities in the alloy would cause a corresponding error in the calculation of the phosphorus content. This of course would render the procedure valueless. Obviously the problem requires for its solution the formulation of methods for the determination of both phosphorus and tin.

PROPERTIES AND USE OF PHOSPHOR-TIN

The phosphorus in phosphor-tin alloys varies as a rule from 0.1 to 5 or 6 per cent. According to Desch,¹ phosphor-tin is grouped with the so-called "brittle alloys," which are described by him as "alloys produced commercially for the purpose of facilitating the addition of small amounts of elements to molten metals. Thus silicon and phosphorus as such are now seldom added to metals, rich alloys of these substances

with iron, copper, or tin being usually employed. These rich alloys are composed principally of inter-metallic compounds, as silicides and phosphides."

Phosphor-tin is manufactured on the large scale by melting tin and phosphorus in large furnaces which are frequently provided with apparatus for the partial exclusion of air. The alloy has a crystalline structure and is very hard and brittle. In color it resembles tin.

This alloy is used instead of tin in the manufacture of various tin alloys for the purpose of either preventing the formation of oxide or enhancing certain mechanical qualities of the alloy into which it enters. For example, in the manufacture of certain bronzes, if phosphorus is added in small amounts, it apparently does not produce, as was originally suspected, a new alloy known as phosphor-bronze. It serves simply as a deoxidizing agent in the molten metal, the resulting phosphoric oxide passing into the slag or scum on the surface.¹ When the metals entering into the composition of the alloy are melted in the absence of phosphorus the alloy is more or less seriously contaminated with oxides. It is obvious, therefore, that if the quantity of added phosphorus be carefully adjusted, the resulting product is merely a purified alloy. However, if a larger quantity of phosphorus is introduced than is required when it is to function simply as a reducing agent the product is an alloy with properties distinctly different from those of the merely purified alloy.

In the manufacture of bronze, according to Desch, "if the quantity of phosphorus introduced through the medium of phosphor-tin exceeds that required for complete deoxidation by more than about 0.1 per cent, it will cause brittleness owing to the separation of hard particles of the phosphide, Cu_3P . Such a mixture is sometimes very incorrectly called phosphor-bronze. If the alloys are to be employed in the manufacture of gear wheels, bearings, etc., the quantities of tin and phosphorus present vary from 6 to 15 per cent and 0.7 to 1.5 per cent, respectively. These alloys are very hard and better able to resist friction. The hardness is due in part to the presence of the hard particles of copper phosphide. The presence of these hard masses in the comparatively soft matrix of lead produces the combination of great hardness with a limited but distinct plasticity which is required for such purposes."

It is not desirable, however, to enter into a detailed account in this paper of investigations in this field of ternary alloys; nor is this necessary to make it perfectly obvious that methods for the rapid and accurate chemical analysis of alloys similar to phosphor-tin are of immediate need in control work.

PRELIMINARY EXPERIMENTS SHOWING THE BEHAVIOR OF THE ALLOY IN CERTAIN SOLVENTS

At the very beginning of this investigation it was concluded that it would be necessary at some stage of the work to determine whether the phosphorus in the alloy is wholly in the chemically combined or uncombined form, although it seemed rather improbable

¹ C. H. Desch, "Metallography," 1910.

¹ Rosenhain, "Introduction to Physical Metallurgy," 1914, 152.