other hydrosols is citrate > oxalate > malate > tartrate > glycolate > succinate = malonate = maleinate > propionate = acetate = fumarate = formate > sulfate > chloride = nitrate, the first named markedly increasing the *p*H value while the last named exerted very slight effect. This effect is ascribed to displacement of coördinatively bound OH groups by the anion of the added salt, the anion then becoming coördinatively bound to zirconium atoms in the micelle. Dialyzed basic zirconium chloride sols become more acid upon standing at room temperature although not so rapidly as basic thorium chloride sols. The decrease in *p*H is hastened by heating and the reactions show no sign of reversal after six months of storage at 25°. In the latter respect, basic zirconium hydrosols differ from those of thorium. As in the cases of other basic metalli-salt hydrosols, the heated sols are less responsive, in so far as *p*H changes, to the action of added neutral salts.

It may be said that "zirconium oxide" hydrosols show a very strong tendency to oxolate.

By application of the ideas which Werner and Pfeiffer suggested for crystalloid basic salts, and assuming that the micelles in basic zirconium chloride hydrosols are polyolated and/or oxolated structures, their behaviors can be readily interpreted.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Extraction of Germanium and Gallium from Germanite. I. The Removal of Germanium by the Distillation of Germanous Sulfide

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Germanite is a sulfide ore containing chiefly copper, iron, arsenic, germanium, zinc, lead, gallium, and aluminum as well as minute amounts of several other elements. It was discovered in 1920 at Tsumeb, South West Africa, by Schneiderhöhn.[2] An analysis by Pufahl[3] showed the presence of germanium, and further analyses by Kriesel,[4] Lunt,[5] and Thomas and Pugh[6] not only verified the germanium but, in addition, showed gallium to be present in appreciable quantities.

Several methods of extraction of germanium from germanite have been reported[7] in which the ore is either roasted or subjected to oxidation with a mixture of nitric and sulfuric acids, leading eventually to the separation of the germanium from aqueous solutions containing the other elements of the ore. The procedures are tedious and require the handling of relatively large quantities of solutions. Patnode and Work[8] chlorinated the ore at 350° and then fractionally distilled the anhydrous chlorides produced. The fraction containing the germanium was hydrolyzed to precipitate the dioxide. After this product had been dissolved in hydrochloric acid, germanium tetrachloride was distilled from the solution in the presence of chlorine, according to the very useful method of Buchanan.[9]

In the present paper, a process is reported for the complete removal of germanium from germanite as germanous sulfide in the vapor phase. The method eliminates the handling of large volumes of solutions, the distillation of liquids, and leaves a residue from which the gallium can be removed very readily. The simplicity of the process will be evident from a description of the operations required for the removal of germanous sulfide.

Operation I.—Finely ground germanite is heated in a stream of dry, oxygen-free, nitrogen gas at 800° with the removal of arsenious sulfide and sulfur.

Operation II.—Ammonia gas is passed over the residue from (I) at 825° whereby the germanic sulfide of the ore is reduced to germanous sulfide, which, in turn, distils from the ore mass to collect in cooler regions of the apparatus. If the arsenious sulfide is completely removed in (I), germanous sulfide is the only substance to leave the ore in (II).

For the preliminary experiments, we are greatly indebted to the late Professor Charles James of

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[2] Schneiderhöhn, *Metall u. Erz*, **17**, 364 (1920).

[3] Pufahl, *ibid.*, **19**, 324 (1922).

[4] Kriesel, *ibid.*, **20**, 257 (1923); *Chem. Ztg.* **48**, 961 (1923).

[5] Lunt, *S. African J. Sci.*, **20**, 157 (1923).

[6] Thomas and Pugh, *J. Chem. Soc.*, **125**, 816 (1924).

[7] Keil, *Z. anorg. allgem. Chem.*, **152**, 101 (1926); Dede and Russ, *Ber.*, **61**, 2451 (1928); and Pugh, *J. Chem. Soc.*, 2540 (1929).

[8] Patnode and Work, *Ind. Eng. Chem.*, **23**, 204 (1931).

[9] Buchanan, *ibid.*, **8**, 585 (1916); *cf.* Müller, THIS JOURNAL, **43**, 1088 (1921); Dennis and Papish, *ibid.*, **43**, 2131 (1921); Dennis and Johnson, *ibid.*, **45**, 1380 (1923).

the University of New Hampshire for a 50-g. sample of germanite. In addition, ore was purchased during the course of the work from the Otavi Minen und Eisenbahn Gesellschaft, Berlin, Germany. Analyses showed the germanium content of the several lots to range from 4.5 to 7%.

Apparatus

A diagram of the apparatus used in the two stages of the process is shown in Fig. 1. A large furnace A was constructed to take care of considerable quantities of the ore, 600–700 g. in *Operation I* and about twice this quantity in *Operation II*. For this furnace, a threaded Vitreosil tube, 56 cm. in length and 7.6 cm. in diameter, wound with number 14 Chromel A wire in two coils of equal length, was placed in a sheet iron container 20 cm. in diameter. The furnace was insulated with Sil-o-Cel. This arrangement permitted use of the coils either in series or in parallel and provided a satisfactory means for controlling the rate of heating and the temperature. The furnace was arranged so that it could be moved horizontally on two steel rods about 1.5 meters in length which were supported at the ends by steel plates. The furnace and carrier were mounted on a bench (not shown in figure).

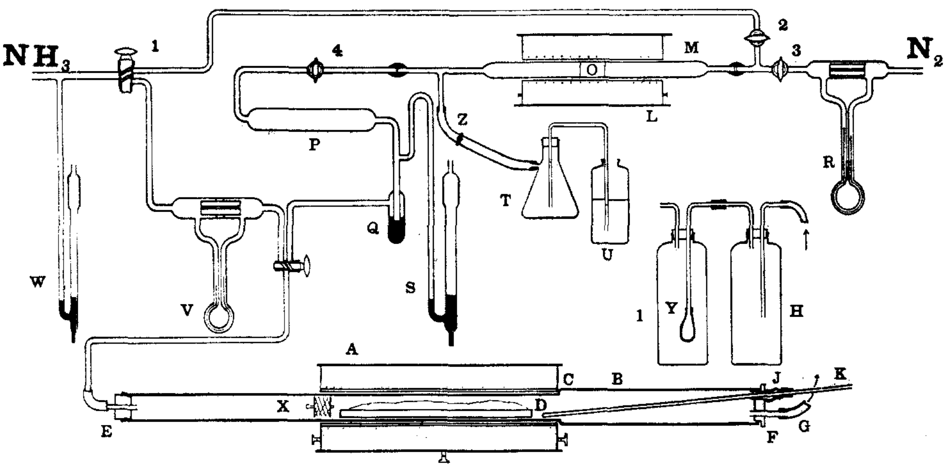

Fig. 1.

The germanite was placed in a cylindrical Alundum boat D, 50 cm. long, 4.5 cm. in diameter and 0.5 cm. thick. The Vitreosil furnace tube B (shown in the figure for *Operation II*) was constructed by fusing a tube, 100 × 5 cm., to a second section, 50 × 10 cm. in dimensions. The joint of the seal at C was made as nearly a right angle as possible. The ends of B were closed with rubber stoppers, E and F; the former being fitted with a glass tube 6 mm. in diameter to permit the entrance of nitrogen or ammonia, while the latter was equipped with a tube G, 15 mm. in diameter, leading to the dust bottles, H and I. A cheesecloth bag, tied at Y, served to remove finely divided material suspended in the gas stream. A large rubber tube led from I to the hood. Through a glass tube J was slipped a loosely fitting Vitreosil tube K, sealed at the inner end and fastened in position with rubber tubing. With this tube it was possible to scrape germanous sulfide crystals from the wall of the large Vitreosil tube B near C to prevent plugging of the apparatus.

For *Operation I*, tube B was replaced by a second Vitreosil tube (not shown in the figure) about 75 mm. long to which was attached by means of an asbestos packed, brass gland an iron tube of the same dimensions. This joint was placed immediately beyond the end of the furnace so that the greater part of the arsenious sulfide condensed in the iron section.

In order to obtain nitrogen free from oxygen, ordinary tank nitrogen was passed over copper wire in the Vitreosil tube M, which was heated to about 600° by an electric furnace L. This tube was provided with a transparent section at O through which one might observe the condition of the copper. After *Operation I*, it was found necessary to reduce the copper oxide in M; ammonia gas was used for this purpose. By proper adjustment of stopcocks 1, 2, 3 and 4, and the screw clamp at Z, the gas stream, which also contained water from the reduction of the copper oxide, was allowed to pass through the trap T and into the bottle U where the excess ammonia was absorbed. A tube P, filled with phosphorus pentoxide, was placed beyond the furnace to dry the nitrogen. The rate of flow of the gas was indicated and regulated by a mercury bubbler Q and a flowmeter R. The apparatus was provided with a mercury safety-trap S which served as an outlet in case of plugging.

The ammonia used in *Operation II* was transferred from commercial cylinders into steel tanks of approximately 10 kg. capacity. The latter contained metallic sodium as drying agent. The ammonia was allowed to escape from these tanks as a gas and to enter the apparatus at a point indicated in the diagram. Its rate of flow was determined by the flowmeter V. A safety-trap W was connected ahead of the furnace tubes. A plug X, made from shredded asbestos held between Chromel wire gauze, was inserted in the furnace tube to prevent heating of the exposed length of quartz tube and circulation of the gases in a direction opposed to the main gas stream. Without this plug considerable material was found to deposit in the cooler regions of the tube in the direction toward E.

Procedure and Results

Operation I.—Between 600 and 700 g. of the ore ground so as to pass through a 100-mesh, but not a 180-mesh, screen was placed in the Alundum boat which was then inserted in the Vitreosil tube. After the air in the apparatus had been expelled by the passage of approximately 50 liters of dry, oxygen-free nitrogen, the furnace was heated to 800° as rapidly as possible, and maintained at this temperature for four and one-half hours with a nitrogen flow of 30 liters per hour. The furnace was allowed to cool and the boat was removed and weighed. After the arsenious sulfide had been scraped from the Vitreosil and iron tubes, another sample was prepared and the above procedure repeated. The resulting slugs were removed from the boat, labeled, and set aside for *Operation II*. The loss in weight for the different lots of ore is recorded in Table I.

TABLE I

LOSS IN WEIGHT OF GERMANITE IN THE TWO OPERATIONS

Ore (lot no.)	Ore, kg.	% loss Operation I	% loss Operation II	Total loss, %
1	8.19	13.6	12.9	26.5
2	17.44	13.6	12.6	26.2
3	24.69	11.9	16.4	28.3
4	19.10	13.2	12.1	25.3
4	4.05	12.6	13.6	26.2
5	16.56	14.0		
5	26.56	15.3	11.1	26.4

Operation II.—Two slugs from (I), equivalent to 1200–1400 g. of the original ore, were placed in the Alundum boat for the second stage of the process. After the plug X was in position, pure nitrogen was passed through the apparatus for fifteen minutes at a rate approaching 60 liters per hour. The furnace was then heated rapidly to a temperature of 825° and kept at this point. Ammonia gas was then admitted at a rate of 50 liters per hour. After a short time, germanous sulfide began to collect at C. Twelve hours of heating was found sufficient to remove all of the germanium. The furnace was allowed to cool, the boat was removed and weighed, and the ore residue was set aside and saved for its gallium content.[10] Tube B was removed from the furnace, the germanous sulfide and metallic germanium were scraped from the walls and separated by hand-picking and screening, and then another charge of the product of *Operation I* was carried through the same procedure.

The loss in weight during *Operation II* is given in Table I. All slugs of ore residue from (I) were numbered and followed through (II) so that the total loss in weight might be known. The loss given in the table for (II) is calculated on the basis of the weight of the original ore.

A complete account of the germanium-containing residues and products and the total amount of germanium found is given in Table II for one lot of ore.

The germanium-containing products were divided into six lots; (1) germanous sulfide crystals, (2) impure germanous sulfide (the chief impurity being metallic germanium), (3) very impure germanous sulfide, (4) germanium-containing dusts, and (5) germanium metal (containing some germanous sulfide as an impurity). All of these products were analyzed for germanium by the usual methods. The impure germanium sulfide shows a higher germanium content than the pure product; this is due to the presence of finely divided metallic germanium, which could not be separated. Analyses of the ore residues (after completion of II) showed the germanium content to range from only 0.04 to 0.05%. On the other hand, the arsenious sulfide distillate, usually amounting to about 10% of the ore, was found to contain between 4 and 5% of germanium. Thus, about 10% of the germanium content of the ore must be recovered from that product.[11]

In the run reported here, product (3) is the largest, but this is accidental; the crystals of pure germanous sulfide were not so coherent and went through the screen in larger percentage. In some runs nearly one-half of the germanium was collected as well crystallized germanous sulfide (1), containing a small amount of metallic germanium, only, as an impurity.

TABLE II

THE AMOUNT OF GERMANIUM OBTAINED FROM GERMANITE (ORE NO. 4, 4.05 KG.)

Type of product	Weight, g.	% Ge	Ge, g.
GeS crystals	68.1	68.1	44.6
Impure GeS	61.2	71.3	43.6
Very impure GeS	157.9	48.8	77.1
GeS in dust bottles	18.3	42.3	7.7
Ge metal	12.8	91.9	11.8
Ge from the tube walls	1.8	69.4	1.3
Ge in As_2S_3 residues	428	4.15	17.8
Ge left in ore	2988.4	0.04	1.2
Total germanium			206.9
% Ge in germanite (based on Ge recovered)		5.11	
% Ge in germanite (based on analysis of 25 g.)		5.13	

Discussion

Attention is called to the fact that the total loss in weight for the combined operations is approximately the same for the different lots of ore, and, in general, it appears that the sum of the germanium and arsenic contents of germanite is very nearly constant. When insufficient time is allotted for (I) more arsenic appears in the products of (II) than would otherwise be the case. With the apparatus described herein, for *Operation I* a nitrogen gas flow of 30 liters per hour, operating for four and one-half hours, was found to be uniformly satisfactory. It is necessary, however, to determine these conditions empirically when working with different lots of ore, since the ratio of the germanium to arsenic varies considerably from lot to lot.

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(10) The recovery of gallium from this residue is described in the following article.

(11) For methods of separating arsenic and germanium, refer to Abrahams and Müller, THIS JOURNAL, **54**, 86 (1932).

In *Operation I* it is essential that the oxygen be removed from the nitrogen. At the temperature of the process, oxygen reacts with germanic sulfide to give germanic oxide. In *Operation II* any germanic oxide in the ore mass would be reduced by the ammonia to metallic germanium which would not be carried out with the gas stream, since its vapor pressure at 825° is exceedingly low. Another precaution which must be observed in (I) is that the temperature should not be permitted to rise much above 800°, as at temperatures ranging from 850-900°, the major portion of germanic sulfide would distil directly from the ore[12] and would be carried along with the arsenious sulfide. Undoubtedly, the germanium found in the arsenious sulfide residues (Table II), even when the temperature is maintained in the neighborhood of 800°, is the result of some distillation of germanic sulfide.

It is apparent that in *Operation II* the germanium leaves the ore mass as germanous sulfide. The presence of a small amount of metallic germanium in the cooler regions of the quartz tube may be attributed to the reduction of germanous sulfide with ammonia in the region of C.

When the furnace has reached the desired temperature, the flow of ammonia gas must be very rapid. If it is too slow, reduction of the sulfide to metallic germanium takes place within the ore before it has an opportunity to get out into the cooler regions. Once the germanium is left in the ore in this condition, its removal can be accomplished only through dissolution with strong oxidizing acids and subsequent distillation of germanium tetrachloride. An ammonia gas flow of 50 liters per hour was found sufficient for the success of (II) with the apparatus described herein.

The only impurity found with the different products of distillation is arsenic, provided all particles of germanite are kept within the region occupied by the furnace. The amount of germanium left in the ore, after the completion of (II), is surprisingly small, approximately 0.5% of the total germanium content. When all of the germanium products and residues are taken into account, the total amount of germanium recovered agrees well with that found by direct analysis.

The procedure described in this article has been used for the extraction of germanium from more than 100 kg. of germanite. The method ensures the removal of at least 99% of the total germanium content. Since only germanium and arsenic in combination with sulfur are removed in the two stages of the process, the ore residues contain all of the gallium.

An advantage of the process is its production of large amounts of nearly pure germanous sulfide, a starting material for the preparation of many compounds of germanium in the lower valence state.[13]

In addition, germanous sulfide is easily oxidized to germanic oxide, which serves as a source for the preparation of germanic compounds. The less pure products are readily converted to pure germanic oxide by the usual methods.

Summary

A method is described which removes at least 99% of the germanium in germanite ore. The procedure is carried out entirely in the dry condition, whereby most of the objectionable features of the usual methods of extraction are eliminated.

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[12] Johnson and Wheatley, *Z. anorg. allgem. Chem.*, **216**, 274 (1934).

[13] Johnson, Morey and Kott, THIS JOURNAL, **54**, 4278 (1932); E. A. Flood, *ibid.*, **55**, 4935 (1933).