XCIX.—Germanium. Part I. The Mineral Germanite and the Extraction of Germanium and Gallium Therefrom.

By JOHN SMEATH THOMAS and WILLIAM PUGH.

DURING recent years the presence of germanium has been detected in minute amounts in various naturally occurring substances; in the mineral waters of Vichy (Bardet, Compt. rend., 1914, **158**, 1278), in euxenite, samarskite, and other complex minerals of this type (Kruss, Ber., 1888, **21**, 131; Chroustchov, J. Russ. Phys. Chem. Soc., 1892, **24**, 30; compare, however, Lincio, Centr. Min., 1904, 142; Dennis and Papish, J. Amer. Chem. Soc., 1921, **43**, **2131**), and in blendes (Urbain, Compt. rend., 1909, **149**, 602; Urbain, Blondel, and Obiedoff, *ibid.*, 1910, **150**, 1758).

The extraction of germanium from the retort residues obtained in the smelting of zinc blendes has been described by Buchanan (J. Ind. Eng. Chem., 1916, 8, 585; 1917, 9, 661), Fogg and James (J. Amer. Chem. Soc., 1919, 41, 947), and Dennis and Papish (loc. cit.).

Gallium is widely distributed in nature in very minute quantities. According to Urbain, it is present in nearly all germanium-containing blendes; it also occurs in bauxite (Boulanger and Bardet, *Compt. rend.*, 1913, **157**, 718) and graphite (Lunt, *Rep. S. African Assoc. Adv. Sci.*, 1923). No mineral, however, has as yet been discovered in which gallium is present in appreciable quantities as an essential constituent. According to Hartley and Ramage (*Proc. Roy. Soc.*, 1896, **60**, 293), the richest source of gallium hitherto known, Middlesbrough cast iron, contains only 1 part of the metal in **33**,000 parts (compare Fogg and James, *loc. cit.*). The only true germanium minerals known are argyrodite and canfieldite, both of which are extremely rare.

In these circumstances, considerable interest attaches to the mineral germanite, recently discovered at Tsumeb, South West Africa, which contains both gallium and germanium in relatively large amounts. This mineral has been described by Pufahl (*Metall und Erz*, 1922, **19**, 324), but he appears to have had only two small pieces of the mineral at his disposal, and his description and more especially his analysis of the mineral are consequently incomplete.

Early in the present year the authors obtained, through the kindness of Professor Andrew Young of this University, about 40 lb. of this mineral, and a more thorough investigation of its nature was undertaken, some of the results of which are described in this paper.

Germanite.

The mineral has a massive crystalline structure and when freshly broken it exhibits a dull lustre. The greater portion of the substance has a characteristic reddish-grey colour, but some pieces are faintly green and highly lustrous. The red portion is not homogeneous; on close examination it is seen to be intimately intergrown with the green substance, which appears to be an arsenical fahlore. Occasionally, also, small, crystalline nodules of a golden-yellow colour may be seen; the quantity of this material is, however, very small. These nodules cannot be scratched with a knife and appear to be iron pyrites. The red material will just scratch fluorspar and its hardness is therefore approximately 4. The finely powdered material-is dark grey in colour and this is also the colour of the streak. The density was found to be 4.59 at 18.5° .

When the powdered mineral was heated in a hard glass tube, a yellow deposit of sulphur condensed in the cool part of the tube, but no decrepitation was noticed. Heated on charcoal before the blowpipe, dense white fumes of arsenic were given off and a slight white incrustation, yellow when hot, was observed, indicating the presence of zinc in the mineral. At very high temperatures the substance fused.

With the exception of nitric acid, acids did not attack the mineral readily in the cold, but when it was treated with moderately strong nitric acid much heat was evolved, nitrogen peroxide was freely

Index to Lines Marked on Plate by means of Dots.

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Strip	Origin	Wave-	Intensity	Strip	Origin	Wave-	Intensity
No.	of line.	length.	in arc.	No.	of line.	length.	in arc.
T	(Ph	3740.20	200	11	Gel.	4226.76	50
-	1 Ĉu	3741.39	- 4		$\left(\frac{\partial}{\partial a} \right)^{\dagger}$	4225.90	1000 r
2	(Mo	3798.41	50 r		Cu	4231.20	
-	Fe	3798.66	10		Mo	$4232 \cdot 82$	10
3	í Cu	3860.61	3		Cu	$4242 \cdot 40$	2 d
<u> </u>	Cu	3861.85	3 d		₹w	$4244 \cdot 52$	5
	Mo	3864.30	50 r		Cu	$4249 \cdot 12$	8
	W	3868·11 f	3		Cu	$4253 \cdot 50$	1 b, d
4	Si	3905.66	15		Cu	$4259 \cdot 57$	2 b, d
5	(Al	3961.67	1000 r		Mo).	$4269 \cdot 47$	4
	(Ca	3968.63 1	300 r		`W ∫1	$4269 \cdot 53$	4
6	(Cu	$4003 \cdot 18$	102	12	(Fe)	4294.30	15
	W	4008.91	10		W / 1	4294.77	10
	l W	4015.39	3		ïWì	$4302 \cdot 28$	8
	(Pb	$4019 \cdot 80$	50		Call	4302.69	100
7	(Mn	4030.92	100 r	13	7 Cu	4507.6	2 b, d
	Gal	$4033 \cdot 18$	30 r		Cu	$4509 \cdot 57$	8
	$\int Mn \langle T \rangle$	$4033 \cdot 22$	100 r		In	4511.35	300 r
	Mn	4034.64	50 r) Cu	$4513 \cdot 40$	1 d
8	ćW	$4074 \cdot 53$	6		S].	$4525 \cdot 25$	1 s
	Cu	4075.75	2		(Fe)T	$4525 \cdot 31$	4
	\mathbf{Sr}	4077.89	1000 r	14	(Cu	$4539 \cdot 9$	3 b, d
	l Cu	4080.70	2		${\rm Si}(vf)$	4552.70	3 s, d
	Mo	$4081 \cdot 62$	5		Ba	4554.21	1000 r
	W	4083.13 2	3	15	(Cu	4674.95	4 d
9	(Bi)	$4121 \cdot 86$	$20 \ d$		Cd	4678.38	50 d
	\mathbf{Fe}	4121.96	1) Zn	4680.30	100
	i Bi	$4122 \cdot 10$	$20 \mathrm{~d}$		Ge	4686.08	$\mathbf{\tilde{5}}$
	Cu	4123.40	$2 \mathrm{~d}$	16	(Cu	4794.3	1 b, d
10	(Ga	$4172 \cdot 22$	30 r		Cu	$4797 \cdot 25^{3}$	1
	l Cu	4177.84	10		í Cd	4800.14	100 r
	C				Zn	4810.76	200
				17	(Mg	5172.86	50
) Mg	5183.79	100
				18	(Mo	5888.50	20
					Na (D.)	5890.19	1000 r
					i Ge ` ´´	5893·8	
					$\ln (D_1)$	5896.16	1000 r
				19	(Li) I	$6708 \cdot 10$	1000 r
					í Cu	$6741 \cdot 15$	12
$\mathbf{r} = \mathbf{reversed}$; $\mathbf{b} = \mathbf{broad}$; $\mathbf{i} = \mathbf{iaint}$; $\mathbf{s} = \mathbf{spark}$ line; $\mathbf{d} = \mathbf{diffuse}$.							
$\parallel = resolved$, $\dagger = unresolved$							

¹ Faint, Fe line involved. ² Faint, Mn line involved. ³ Faint, V line involved (?).

given off, and, with the exception of a small residue consisting mainly of silica, lead sulphate, and germanium dioxide, the mineral dissolved.

A spectroscopic examination of the mineral was made by Dr. J. Lunt of the Royal Observatory, Cape Town (see South African J. Sci., 1923, 20, Part I) and this revealed the presence of the following 26 elements: copper, sulphur, iron, lead, arsenic, germanium, zinc, tungsten, gallium, silicon, molybdenum, manganese, cadmium,



aluminium, magnesium, barium, strontium, calcium, vanadium, titanium, nickel, cobalt, bismuth(?), indium, lithium, sodium, silver. The authors are indebted to Dr. Lunt for the accompanying photograph, from the above-mentioned paper, of the spark spectrum of the mineral (see also Table), which shows some of the most characteristic lines exhibited by the various elements present therein. Of the elements detected spectroscopically, the presence of the following has also been established by the usual analytical methods and they have been quantitatively estimated. The figures given are the mean of three concordant determinations. Cu 44.01; S 30.96; Fe 5.08; As 6.83; Ge 5.10; Zn 2.74; Pb 2.26; Ga 0.57; W 0.03; Mo trace; Au trace; insoluble (SiO₂) 1.84; (BaSO₄) 0.02; total per cent. 99.44.*

Some Notes on the Analysis of the Mineral.

A fair sample of about 200 grams was taken from about 10 kilograms of the finely powdered mineral, and portions of this sample were taken for analysis as required. The substance was most conveniently decomposed by means of a mixture of nitric acid (25 c.c.), sulphuric acid (10 c.c.), and water (25 c.c.). For the estimation of the metals contained in the mineral in considerable quantity, including germanium, about 5 grams of the finely powdered substance were treated with the quantity of mixed acid indicated above. The first vigorous reaction was controlled by cooling and after it had ceased the mixture was gently heated for several hours in order to remove nitric acid. In one or two instances, the residue contained tiny, yellow specks; they were suspected to be gold, and when tested they gave a distinct purple of Cassius reaction, a result subsequently confirmed independently (see previous footnote). The solution, together with the residue, was transferred to a small flask fitted with a short distillation column, cooled, saturated with chlorine, concentrated hydrochloric acid added, and the mixture distilled in a current of chlorine, the distillate being collected in well-cooled water. It was necessary to maintain a high concentration of hydrochloric acid in the distilling flask,

^{*} Since this analysis was made the authors have learned through Dr. Lunt that the resident chemist at the mine, Herr F. W. Kriesel, has also carried out an analysis on carefully selected pieces of the ore. According to him its composition is as follows: Cu, 4539; Pb, 0.66; Zn, 2.58; Fe, 4.56; Ge, 8.70; As, 4.13; S, 30.65; Ga, 0.76; SiO₂, 0.226; WO₃, 0.184; TiO₂, 0.004; Mo, 1.282; Mn, 0.020; Ni, 0.001; Co, 0.013; Cd, 0.071; CaO, 0.122; MgO, 0.055; C, 0.136; total 99.544 per cent.

The divergence between these figures and those obtained by the authors is probably explained by the fact that whereas Kriesel examined selected pieces, the authors worked on an average sample of the mineral.

otherwise, as Dennis and Papish have pointed out, the germanium tetrachloride underwent hydrolysis and was not completely driven These authors state that in this way a complete separation over. of germanium from arsenic can be effected, but in this investigation small quantities of the latter were invariably found in the distillate. After passing hydrogen sulphide through the liquid which condensed, the precipitated sulphides were collected and redistilled in the same manner. No arsenic was found in the second distillate. \mathbf{It} would appear, therefore, that this separation is only complete in one operation when the amount of arsenic present is relatively small. Nevertheless, the criticism by Dennis and Papish of Muller's views on this question (J. Amer. Chem. Soc., 1921, 43, 1085) seem to the present authors to be fully justified. Finally, the germanium in the distillate was precipitated as sulphide by means of hydrogen sulphide. Sulphuric acid had been previously added, whenever necessary, in order to bring the acid concentration to approximately 6N. Germanium disulphide separated as a pure white, flocculent precipitate, which was collected after twenty-four hours, washed with 5N-sulphuric acid saturated with hydrogen sulphide until free from hydrochloric acid, dried, treated with concentrated nitric acid, converted into the dioxide by ignition, and weighed The removal of the last traces of sulphuric acid presented as such. some difficulty. This was accomplished by moistening the substance, after the first ignition, with ammonia and again heating strongly. The dioxide obtained in this way was a heavy, soft, white powder.

After the separation of the germanium, chlorine was removed from the flask by a current of carbon dioxide, the arsenic reduced with sulphur dioxide, fresh hydrochloric acid added, and the liquid was distilled until only a small amount remained. The distillate of arsenic trichloride was collected in well-cooled water, the greater part of the sulphur dioxide removed by carbon dioxide, and the arsenic precipitated as As_2S_3 , which was weighed after the usual treatment.

The liquid remaining in the distilling flask was filtered, the lead sulphate extracted from the residue in the usual way, and the silica estimated. The very small residue obtained, which was believed to be barium sulphate, was examined by Dr. Lunt and found to produce a pronounced barium line.

Copper, lead, iron, zinc, and tungsten were estimated in the solution by standard gravimetric methods. A separate portion of the mineral was taken for the estimation of sulphur. In this case, decomposition was effected by means of nitric acid and bromine. After evaporating off the excess of nitric acid, the lead sulphate was collected and weighed and the remaining sulphur converted into barium sulphate in the usual way and weighed as such.

For the estimation of gallium 50 grams of the finely powdered mineral were decomposed by means of the mixture of nitric and sulphuric acids previously mentioned. After the free nitric acid had been removed by evaporation, sulphur dioxide was passed through the solution, 100 c.c. of concentrated hydrochloric acid were added, and the liquid was distilled. Arsenic and germanium were thus volatilised as chlorides. The residue was diluted with water and kept, when the greater part of the lead separated as lead sulphate, which was removed, together with the insoluble residue, by filtration. To the solution (about 300 c.c.) 10 c.c. of concentrated nitric acid were added and the copper was precipitated electrolytically. The solution was then evaporated with hydrochloric acid in order again to remove the nitric acid, after which it was saturated with hydrogen sulphide and kept for some hours. A faint brown precipitate formed, consisting probably of traces of lead, arsenic, and copper.

Ammonium hydroxide was then added to the solution until a slight permanent precipitate was obtained and the mixture was boiled with zinc under a reflux condenser for four hours. The precipitate so obtained was collected, dissolved in hydrochloric acid, the solution made strongly alkaline with sodium hydroxide, and zinc removed as sulphide. The filtrate was strongly acidified with hydrochloric acid, potassium ferrocyanide added, and the gallium, which is completely precipitated as ferrocyanide under these conditions, was treated according to Browning and Porter's method (*Amer. J. Sci.*, 1917, **44**, 221), being ultimately weighed as the oxide Ga_2O_3 , which was obtained as a white powder insoluble, after ignition, in acids.

The Extraction of Germanium.

The method employed for the extraction of germanium from the mineral was based on that first described by Buchanan (J. Ind. Eng. Chem., 1917, 9, 661) and improved by Dennis and Papish (loc. cit.). The main difficulty encountered arose from the relatively large amount of arsenic present in the substance. The process for the separation of these elements described above was not successful, and no better results were obtained when potassium dichromate was added to the solution (Browning and Scott, Amer. J. Sci., 1918, 46, 663); the methods of fractional precipitation employed by Winkler (J. pr. Chem., 1886, 142, 194), and by Urbain, Blondel, and Obiedoff (loc. cit.) were unsatisfactory also.

Ultimately it was found best to remove arsenic as completely

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as possible as a preliminary operation by roasting the mineral in a muffle furnace in a current of air. Lots of 100 grams of the finely powdered mineral were heated on shallow clay dishes until the weight remained constant. The loss of weight usually amounted to about 11 grams. When the mineral was roasted at high temperatures, the yield of germanium obtained was invariably small, and it appeared to vary inversely with the temperature at which the roasting had been carried out. In one case, in which the furnace was heated to bright redness, the substance being sintered, scarcely any germanium was obtained. The best results were obtained when the mineral was roasted at a dull red heat, approximately 500°, for about six hours; further heating at this temperature produced no further loss of weight, and very little arsenic remained in the mineral. The powder was then treated with hydrochloric acid and the solution distilled.

In the actual distillation Dennis and Papish's method was followed closely except that the liquid was first saturated with chlorine and a stream of this gas was kept passing through it during the distillation. The amount of mineral dealt with in each operation was limited to quantities not exceeding 200 grams. The germanium tetrachloride was collected in water, in which it underwent hydrolysis to hydrated germanium dioxide. This was filtered off, washed free from hydrochloric acid, and ignited; the product was free from arsenic. The acid concentration of the filtrate was adjusted to approximately 6N by addition of sulphuric acid, germanium sulphide containing traces of arsenic was precipitated with hydrogen sulphide, and the precipitate was washed with 5N-sulphuric acid saturated with hydrogen sulphide, dried, and roasted at a dull red heat for three hours. A second distillation was carried out in the same way, but the sulphide was in this instance treated with nitric acid and finally ignited.

The germanium dioxide obtained by this method was pure white in colour and free from arsenic. The average yield amounted to about 92 per cent. of the theoretical.

The Extraction of Gallium.

The main difficulty in the recovery of the gallium from the accumulated residues from the extraction of germanium arose from the very large amounts of copper and other heavy metals in the material to be treated, compared with the quantities of gallium present. The method involving preliminary complete removal of these metals was costly and tedious, and the following cheaper and quicker process was adopted.

The residues were filtered off, the solid was washed with water,

the combined filtrate and washings were diluted until 1 litre of solution was obtained for each 50 grams of mineral originally taken (this dilution is essential), and to the solution, heated to boiling, ammonium hydroxide was added until a permanent precipitate was obtained, which was collected after two hours' boiling. It consisted mainly of copper hydroxide together with small quantities of hydroxides of iron and other heavy metals, and it also contained practically all the gallium. However, in order to make certain that no gallium was lost, the filtrate was again treated in a similar manner and the precipitate obtained was combined with the first. This preliminary operation effected a very considerable concentration of the gallium with a corresponding economy of time and material.

The precipitate was now dissolved in hydrochloric acid and through the fairly strongly acid solution hydrogen sulphide was bubbled until no further precipitate formed; when the hydrogen-ion concentration was too low, a tendency was observed for gallium to be carried down with the precipitate. The best results were obtained with approximately 6N-acid, dissolution and reprecipitation of the sulphide precipitate then being unnecessary. This precipitate, consisting mainly of copper sulphide together with small quantities of sulphides of other metals of the copper group, was filtered off and washed with hydrogen sulphide solution until the washings were free from chloride-ions.

For the separation of gallium from this solution two methods gave good results. In one method, potassium ferrocyanide was added to the strongly acid solution, the precipitate, consisting of ferrocyanides of gallium and iron, was filtered off, dried, ignited in a platinum capsule, the residue fused with a small quantity of sodium hydroxide, and the solid mass thus obtained extracted several times with small quantities of water. This solution was neutralised with hydrochloric acid, made faintly alkaline with ammonium hydroxide (1 c.c.), and boiled, a gelatinous precipitate of gallium hydroxide being thrown down. After the liquid had boiled for about half an hour and all the ammonia had been driven off, this precipitate was filtered off, washed with ammonium nitrate solution, dried, and ignited to gallium oxide, which was obtained as a pure white powder. This precipitation of gallium hydroxide by the addition of ammonia is quantitative, and was employed by Lecoq de Boisbaudran (Ann. Chim. Phys., 1884, [vi], 2, 181) for the estimation of the element.

Although this method yielded very pure gallium oxide, it has certain disadvantages. In the first place the ferrocyanide precipitate is difficult to filter and the process is consequently slow. Then, as Dennis and Bridgman have pointed out (J. Amer. Chem. Soc., 1918, 40, 1531), when gallium hydroxide is precipitated by means of ammonia it adheres to the glass of the vessels employed in a remarkable manner, and its complete removal can only be effected with the greatest difficulty. For these reasons, an alternative method of treatment was worked out.

The process finally adopted was based on the great extent to which gallium salts undergo hydrolysis in aqueous solution. The solution remaining after the removal of the sulphide precipitate was neutralised with ammonia and water was added until 500 c.c. of the solution contained roughly 0.1 gram of gallium. The liquid was then faintly acidified with a few drops of hydrochloric acid, about 3 grams of sodium thiosulphate were added, and the solution was boiled vigorously for five minutes. Sulphur dioxide was evolved and a copious precipitate consisting of gallium hydroxide mixed with sulphur was formed. This was filtered, washed with ammonium nitrate solution as in the previous method, and redissolved in hydrochloric acid. Gallium hydroxide was then reprecipitated by the addition of sodium thiosulphate in the manner already described. The precipitate was filtered, washed, dried. and, after treatment with a few drops of concentrated nitric acid to oxidise the sulphur, ignited. Pure white gallium oxide was thus obtained. The reprecipitation described above was rendered necessary by the presence of a trace of iron in the first precipitate.

The sulphur precipitated simultaneously with the gallium hydroxide does not amount to a disadvantage. On the contrary, when the precipitation is carried out in this manner the tendency of the hydroxide to adhere to the vessel is greatly diminished. Further, the precipitate is distinctly granular and filtration is consequently facilitated. The removal of the sulphur by oxidation with nitric acid presents no difficulty.

The yield obtained in each case was very good and corresponded closely with the amount obtained in the analysis of the mineral.

The Preparation of Metallic Germanium.

According to Winkler (J. pr. Chem., 1887, [ii], **36**, 188), germanium dioxide, when heated to red heat in a current of hydrogen, undergoes reduction to the metal, but he states that the reduction does not always proceed to completion. As a specimen of the metal was required in connexion with certain projected investigations, amongst which an examination of the spectrum of the element and especially the determination of its crystal structure * may be mentioned,

* This has been undertaken by Professor A. Ogg of this University, and a communication on this subject may shortly be expected.

an attempt was made to prepare metallic germanium by Winkler's method. The results were not very satisfactory in that it was found impossible to obtain the element in a coherent form. Since these experiments were made, the reduction of germanium dioxide by hydrogen has been studied by Dennis, Tressler, and Hance (J. Amer. Chem. Soc., 1923, 45, 2033), whose account agrees closely with the authors' observations, which need not therefore be recorded here.

Dennis, Tressler, and Hance fused powdered germanium, obtained by the reduction of the dioxide by hydrogen, with sodium chloride as a flux and obtained buttons of the element of considerable size. They have thus been able very fully to investigate the physical and chemical properties of the metal.

The reduction of germanium dioxide by hydrogen can only be satisfactorily carried out in small quantities. This method of preparing the metal is therefore necessarily slow and tedious, and was abandoned by the present authors.

It is well known that tin is quantitatively obtained when stannic oxide is reduced by means of potassium cyanide, either with or without the addition of carbon, and the preparation of germanium was therefore attempted along these lines. Five grams of germanium dioxide which had previously been ignited were mixed with 35 grams of a mixture of potassium cyanide and powdered charcoal. The flux was also dried beforehand. The mixture was placed in a crucible which was covered with a well-fitting lid and was then introduced into a muffle furnace, heated at approximately 1000°. After half an hour, the crucible was withdrawn, tapped, and allowed to cool. On breaking it open, a beautifully crystalline button of germanium was found, the weight of which was 90.3 per cent. of the calculated amount. The remainder was present in the flux as potassium germanate and was recovered. The fused mass was dissolved in water and filtered. The liquid was then acidified with sulphuric acid and from this strongly acid solution germanium disulphide was precipitated in the usual manner.

Similar experiments were carried out in which potassium cyanide without the addition of carbon was used as the flux, and the results obtained are of some little interest. In the first of these experiments, commercial cyanide containing a considerable amount of free alkali was employed, and it was not specially dried. As before, the weight of flux used was about six times that of the germanium dioxide taken. On introducing the crucible into the furnace, the mixture frothed and white fumes were observed in the furnace. The crucible was withdrawn from the furnace after half an hour and allowed to cool. On breaking it, a button of the metal was obtained, but its 826

weight was only 41 per cent. of the calculated amount. The greater part of the germanium remained in the flux as potassium germanate and was subsequently recovered. The amount of germanium unaccounted for was small and the fumes observed could not have been attributable entirely to germanium compounds. In a second experiment carried out in a precisely similar manner, the purest potassium cyanide at hand was employed, and it was carefully dried before use. In this case much less frothing occurred and very little fume was observed in the furnace. The weight of the button obtained was 77 per cent. of that calculated. A final experiment was then made in which a mixture of charcoal with the purest potassium cyanide available was used as the flux. In this case, the weight of the button was 95.4 per cent. of the calculated amount. Thus it appears that the mixture of potassium cyanide and carbon referred to is the most suitable reducing agent for the preparation of germanium, and that its efficiency depends in great measure on the purity of the potassium cyanide employed. The frothing and fuming observed when potassium cyanide alone was employed seem to have been due to the presence of water and of free alkali.

Summary.

1. An account has been given of the mineral germanite from Tsumeb, S.W. Africa.

2. This mineral was found to contain 5.1 per cent. of germanium and 0.57 per cent. of gallium. An analysis of selected pieces of the mineral seems to indicate that the percentage of these elements may be considerably higher.

3. The methods employed for the estimation of germanium and gallium and for the extraction of these elements from the mineral have been described.

4. The reduction of germanium dioxide by means of potassium cyanide alone and by mixtures of potassium cyanide with carbon have been investigated. The purity of the potassium cyanide used was found to be an important factor in determining the yield of germanium obtained. Using a mixture of pure potassium cyanide and wood charcoal as the reducing agent, a yield of 95 per cent. has been obtained.

In conclusion, the authors desire to express their sincere thanks to Professor Andrew Young, who presented the mineral to them, and to Dr. J. Lunt and Herr F. W. Kriesel for help and valuable information given during the progress of the work.

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