[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

GERMANIUM. XXV. ARC SPECTROGRAPHIC DETECTION AND ESTIMATION OF GERMANIUM. OCCURRENCE OF GERMANIUM IN CERTAIN TIN MINERALS. ENARGITE AS A POSSIBLE SOURCE OF GERMANIUM[1]

BY JACOB PAPISH, F. M. BREWER AND DONALD A. HOLT

RECEIVED AUGUST 2, 1927 PUBLISHED DECEMBER 10, 1927

Arc Spectrographic Detection and Estimation of Germanium

The emission spectrum of germanium contains a number of persistent lines which, as is the case with all metals and with a few non-metals, lie in the optical spectral range. These lines serve admirably for the detection of small quantities of germanium, and in connection with some of the less persistent lines they can be used in the quantitative estimation of this element. A direct current arc of about half a kilowatt made between two electrodes of pure graphite was used for spectral excitation. The spectrograms were prepared with the aid of a quartz spectrograph of the Littrow auto-collimating type[2] using double-coated ortho photographic plates.[3] 1.4408 g. of pure germanium dioxide was introduced into water, solution being effected with the aid of the least amount of potassium hydroxide, and the volume was made up to 100 cc., thus furnishing a solution containing an equivalent of one gram of germanium per 100 cc. From this stock solution, solutions containing 0.1, 0.01, 0.001, 0.0001 and 0.00001 g. of germanium per 100 cc. were prepared. The arc discharge was passed between the graphite electrodes for a few moments; it was then interrupted, to allow the electrodes to cool somewhat, and while the latter were still warm, a small, definite portion of each solution was placed on the lower electrode. These portions consisted of one-tenth cc. of solution and were delivered from a calibrated capillary pipet holding in all 0.12 cc. and divided into fiftieths of a cubic centimeter. Different electrodes and a separate plate were used for each concentration, one spectrogram of the blank arc and four of the arc charged with the germanium material being obtained on a single plate. The charges actually placed on the lower electrodes contained 1, 0.1, 0.01, 0.001 and

---

[1] The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

This article is respectfully dedicated by the authors to Professor L. M. Dennis, and will be reprinted as Article No. 6 in the Louis Munroe Dennis Quarter Century Volume to be published in 1928 in commemoration of the completion by Professor Dennis of twenty-five years of service as Head of the Department of Chemistry at Cornell University.

[2] Made by Adam Hilger, Limited, London.

[3] Made by Eastman Kodak Company, Rochester, N. Y.

0.0001 mg. of germanium, respectively. The spectral lines observed at the different concentrations are given in Table I. In this table, as well as in those that follow, v signifies that the line in question is visible and f that it is faintly visible. The decrease of intensity has been brought about by the decrease of the quantity of material in the zone of excitation. The investigation was limited to the spectral range between λ 4682 and λ 2198 Å.

Table I

Spectral Lines at Different Concentrations

λ	1 mg.	0.1 mg.	0.01 mg.	0.001 mg.	0.0001 mg.
4685.9	f				
4226.6[a]	v	v	v	v	
3269.5	v	v	v	f	
3124.8	v	v			
3067.0	v	v			
3039.1	v	v	v	v	v
2829.0	v	f	f		
2793.9	v				
2754.6	v	v	v	v	
2740.4	v	v			
2709.6	v	v	v	v	
2691.3	v	v			
2651.6	v	v	v	v	f
2651.1[b]	v	v	v	v	v
2644.2	v	v			
2592.5	v	v	v	v	
2589.2	v	f			
2556.3	v				
2533.2	v	v			
2498.0	v	v			
2436.4	v				
2417.4	v	v	v	f	
2397.9	f				
2394.1	f	f			
2359.2[c]	v	v	f		
2338.6	f	f			
2327.9	f				
2314.2	v	f			
2198.7	v	f			

[a] Because of the low dispersion of a prism spectrograph in this range, λ 4226.6 of germanium is indistinguishable from λ 4226.7, a persistent line of calcium.

[b] C. W. Gartlein of the Department of Physics, Cornell University, found that the wave length of this line is 2651.2 Å.

[c] The wave length of this line was determined by C. W. Gartlein.

If germanium in any form in quantities larger than one milligram, be subjected to arc excitation, λ 2389.5, λ 2379.1, λ 2256.0 and λ 2246.4 will be visible in addition to the lines included in Table I. As seen from this table λ 3269.5, λ 2754.6, λ 2709.6 and λ 2417.4 are visible when 0.001 mg. of germanium is introduced into the arc, while λ 3039.1, λ 2651.6 and λ 2651.1 persist when one-tenth of this quantity is used. The *raies ultimes* of de Gramont[4] are among these lines.

Occurrence of Germanium in Certain Tin Materials

Germanium-tin mixtures were prepared by mixing water solutions of germanium dioxide and stannous chloride in such proportions as to have 0.0001 mg. of germanium with tin varying in quantity from 0.01 mg. up to one milligram. Similar mixtures with higher germanium concentrations, using fixed alkali germanates, were also prepared. As ex-

---

[4] De Gramont, *Compt. rend.*, **171**, 1106 (1920). See also Foote and Mohler's "The Origin of Spectra," The Chemical Catalog Company, Inc., New York, **1922**, p. 143.

pected, the presence of tin had no influence upon the spectral lines of germanium except in cases of lowest germanium concentration. When 0.0001 mg. of this element in a mixture with tin was subjected to spectral excitation, the persistent lines of germanium were much fainter than when germanium alone is used. Twelve tin minerals[5] were subjected to arc spectrographic examination for the presence of germanium in the following manner. They were ground finely and definite quantities of each were introduced into the arc. These quantities varied from 6 to 10 mg. Several successive exposures were obtained from each mineral sample without replenishing the arc with fresh material; in this way it was observed that in the case of some of the minerals lines due to germanium were present in the first spectrogram only, while in the case of others they also appeared in those that followed. The results which were obtained from an examination of the spectral range between λ 3040 and λ 2590 are summarized in Table II.

Table II

Germanium Lines in Spectrograms of Tin Minerals

Range examined, λ 3040–λ 2590

Mineral and source	3039.1	2651.6	2651.1	2592.5	% Ge, estd.
Cassiterite, San Joge Mine, Loyaza, La Paz, Bolivia	v	f	f	..	0.001
Stream tin, Buck Creek, Alaska	..	..	..	..	Absent
Cassiterite, north of Battle Mountain, Nevada	v	v	v	v	More than 0.005
Cassiterite, Clive County, Mole River, New England, N. S. W.	v	f	f	..	0.001
Cassiterite, Ena Mino, Japan	f	..	..	..	Negligible
Cassiterite, Burra Tumbarumba, N. S. W.	..	..	..	..	Absent
Cassiterite, Hot Springs, Lower Tanana River, Alaska	f	..	..	..	Negligible
Cassiterite, Cornwall, England	f	..	..	..	Negligible
Stream tin, Durango, Mexico	v	v	v	f	0.005
Wood tin, Dawson, Yukon Territory	v	f	f	..	0.001
Cassiterite, Bakerville, Queensland	..	..	..	..	Absent
Cassiterite, King Mountain, North Carolina	..	..	..	..	Absent

Eight of the twelve tin minerals subjected to spectrographic analysis were found to contain traces of germanium. The estimated percentage of germanium in these minerals, which is given in the last column of Table II, was obtained as follows. A record was made of the spectral lines of germanium as observed in connection with each mineral. It was then assumed that a definite weight of germanium, say in milligrams, capable of yielding these particular spectral lines was present in the zone of excita-

---

[5] Kindly supplied by Dr. David White of the U. S. Geological Survey.

tion. Knowing the quantity of each mineral subjected to excitation it was a simple matter to estimate its germanium content. This method has been found in our Laboratory to give fairly satisfactory results in a good many cases where the element to be estimated quantitatively is present in traces. It is important that minimum quantities of the crude material or mixture containing the element in question be introduced into the arc.

TABLE III

GERMANIUM LINES IN SPECTROGRAMS OF ENARGITE

(Range examined, λ 3040–λ 2498)

Enargite No.	3039.1	2754.6	2740.4	2709.6	2691.3	2651.6	2651.1	2644.2	2592.5	2589.2	2533.2	2498.0	% Ge, estd.
1	v	v		v	f	v	v	f	v			v	More than 0.01
2	f					f	f						Less than 0.001
3													None
4	v	f		f		v	v		f				More than 0.001
5	v	v		v		v	v		v			f	0.01
6	v	v		v		v	v		v			f	0.01
7	v	v		v	f	v	v	f	v			f	More than 0.01
8	f												Negligible
9	v	v		v		v	v		v				0.01
10	v					f	f						Less than 0.001
11	v	v	v	v	v	v	v	f	v	f	f	v	More than 0.1
12	v	v		v	f	v	v	f	v			f	0.01
13	v	f		f		[a]	[a]		f				More than 0.001
14	v	v	v	v	v	v	v	f	v	f	f	f	0.1
15	v					f	f						Less than 0.001
16													None
17													None

No. 1. Enargite from Central City, Colorado.
No. 2. Enargite from Butte, Montana.
No. 3. Enargite from Ouray County, Colorado.
No. 4. Enargite from Butte, Montana.
No. 5. Enargite from Butte, Montana.
No. 6. Quartz and pyrite gangue from No. 5.
No. 7. Enargite from Braden Copper Company, Chile.
No. 8. Pyrite gangue from No. 7.
No. 9. Enargite from Red Mountain, Ouray County, Colorado.
No. 10. Gangue material from No. 9.
No. 11. Enargite from Santa Fé Mine, Chiapas, Mexico.
No. 12. Enargite from Shoebridge Lode, Tintic District, Utah.
No. 13. Enargite from Rising Star, Nevada.
No. 14. Enargite from Butte, Montana.
No. 15. Enargite from Shoebridge Lode, Tintic District, Utah.
No. 16. Pyrite gangue from No. 15.
No. 17. Enargite from Montana.

[a] Because of the extremely high lead content of this ore, the lead line λ 2651.7 was so wide that it completely obstructed the two germanium lines λλ 2651.5 and 2651.1.

Enargite as a Possible Source of Germanium

Enargite is a fairly common copper-bearing mineral in which this element is combined with arsenic and sulfur and associated with traces of other elements. Specimens of this mineral from various localities were investigated spectrographically for the presence of germanium. The method followed was similar to the one used in connection with the tin minerals and the results are recorded in Table III.

Since some of these ore minerals were available in comparatively large quantities, work was undertaken to extract germanium from them. The ore was ground finely, placed in a Pyrex distilling flask and decomposed with nitric acid. The contents were heated to dryness over a steam-bath, sulfuric acid was added and heat was applied until the oxides of nitrogen were driven off. Hydrochloric acid was then added and the whole saturated with chlorine and distilled in a slow current of this gas. Samples of the residue were tested from time to time spectrographically for the presence of germanium and the distillation was discontinued when germanium was found to be totally absent or present in negligibly small traces. The distillate which contained germanium tetrachloride was collected in a cooled receiver and saturated with hydrogen sulfide. The germanium disulfide thus obtained was removed and converted to the dioxide.

The method developed by Dennis and Johnson[6] was used to determine germanium quantitatively in some of the enargite ores. It was necessary, however, to modify this method slightly in its initial stage. The weighed sample of enargite was decomposed in the manner just described in connection with the extraction of germanium from this mineral. The residue, freed from the oxides of nitrogen, was subjected to the hydrochloric acid-chlorine distillation. Determinations made on two samples of enargite gave the following results:

	Enargite No. 1	Enargite No. 5
Weight of enargite	50 g.	100 g.
Weight of GeO_2 extracted	0.0238 g.	0.0192 g.
Percentage of germanium	0.033	0.013

The enargite minerals dealt with in the present investigation contained much less germanium than the rare minerals argyrodite, canfieldite and germanite. Nevertheless, enargite, because of its availability, can be used as a source of this element. In school laboratories where students do experimental work with the so-called rarer elements, enargite can be made to serve as the crude material from which to extract germanium. In view of the variation of the germanium content in the different samples of enargite, it is possible that some enargites not as yet investigated are considerably richer in germanium. Ordinary copper of commerce is

[6] Dennis and Johnson, THIS JOURNAL, **47**, 790 (1925).

known not to contain germanium, and since large quantities of copper are obtained from enargite, it is not impossible that at some stage of smelting or refining the germanium contained in the ore is concentrated in some waste product or by-product. We know that this happens in the case of certain zinc ores containing minute traces of germanium; these traces are increased to a very appreciable content in a by-product during the process of smelting.[7] It is our intention to extend the present investigation to copper smelter materials in hope of finding germanium in a form more concentrated than in the original enargite.

Summary

The arc spectral lines of germanium and the concentrations at which they appear were given.

The presence of traces of germanium in certain tin ores was noticed.

A method was given for the estimation of traces of germanium.

Germanium was found to be present in appreciable traces in certain varieties of enargite.

A method for the extraction of germanium from enargite was described.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE INFLUENCE OF RADIATION ON THERMAL UNIMOLECULAR REACTIONS

BY JOSEPH E. MAYER

RECEIVED AUGUST 12, 1927 PUBLISHED DECEMBER 10, 1927

Introduction[1]

The concept of molecules of high energy content as the reacting molecules in chemical reactions was first introduced by Arrhenius[2] primarily to explain the high temperature coefficient of most reactions. Although this theory has been generally accepted, there has been considerable dispute as to whether the mechanism of activation is by collisions between molecules or by the absorption of radiation. The radiation hypothesis, first suggested in a rather vague form by Trautz[3] and later elaborated by W. C. McC. Lewis[4] and by Perrin[5] appeared to be much strengthened by

---

[7] See Buchanan, *J. Ind. Eng. Chem.*, **8**, 585 (1916); Dennis and Papish, *Z. anorg. Chem.*, **120**, 1 (1921).

[1] A brief statement of the results of this investigation (excepting the last and most convincing experiment) has been published in a paper by G. N. Lewis and J. E. Mayer, *Proc. Nat. Acad. Sci.*, **13**, 623 (1927).

[2] Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

[3] Trautz, *Z. wiss. Phot.*, **4**, 160 (1906).

[4] W. C. McC. Lewis, *J. Chem. Soc.*, **109**, 796 (1916); **111**, 457 (1917); **113**, 471 (1918).

[5] Perrin, *Ann. phys.*, [9] **11**, 1 (1919).