

age was held constant when at work by means of the volt meter and rheostat. The bar was of wood and carefully graduated to sixteenths of an inch. Its base served as a track for the Lummer-Brodhun sighting box to run on. The bar was 8 feet long with the electric lamp at zero. The distance from the other end of the bar to the street light was measured by means of a light stick, with a pointer at one end of it and a fork at the other, large enough to span the lamp. Each prong of the fork terminated with a ring with a wire cross-hair stretched across it. This afforded an easy and accurate means of getting the distance from the center of the mantle to the end of the bar, which of course, varied with the different lamps.

The instrument required two men to operate it; one to adjust the bar and take the reading and the other to line up the cross hairs with the mantle and get the distance from the bar. The time required to back up to a lamp, adjust the bar, take the readings and measurements and get away was about seven minutes. The candle power of the lamps for each night's work was figured out afterwards by means of logarithms and a table of squares.

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CONTRIBUTIONS TO THE CHEMISTRY OF THALLIUM, II.

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A New Method for the Gravimetric Determination of Thallium. By precipitating and weighing the thallium as thallium sulphostannate, $Tl_4SnS_4^1$, a very accurate and easy determination of thallium can be made. The thallium sulphostannate can readily be prepared in pure condition; it is practically insoluble in water so that it can be washed very thoroughly without loss, and it can be dried at 105° without decomposition. The thallium may be in either the thallos or thallic condition at the time of precipitation since the precipitants will also act as reducing agents. All the elements precipitated by sodium sulphide, including those which are soluble in excess, will interfere with the formation of pure thallium sulphostannate. The reagents required are a solution of primary sodium sulphide with a concentration of about 150 grams per liter, and a solution of sodium sulphostannate containing only a slight excess of sodium sulphide. This latter solution need not be free from the sodium salts formed in its preparation and can therefore readily be made by adding sodium sulphide solution to a solution of stannic chloride until the precipitate first formed is just dissolved. The procedure for the preparation of the pure thallium sulphostannate is as follows:

To the hot and very slightly acid solution of the thallium salt add an excess of the sodium sulphostannate solution, *i. e.*, more than enough to form

¹ Hawley, J. Physic. Chem., 10, 654 (1906).

Tl_4SnS_4 with all of the thallium present. The precipitate now consists of Tl_4SnS_4 and the solid solution with excess of stannic sulphide¹; if the solution is still acid there is also some thallium unprecipitated. Add the primary sodium sulphide solution drop by drop with constant stirring until the solution is neutralized, then add at once 25 cc. more and heat to boiling. Boil slowly for five minutes, stirring with a rod held against the bottom of the beaker to prevent bumping. This boiling in the presence of the primary sodium sulphide solution dissolves any stannic sulphide in excess of the formula Tl_4SnS_4 . A slight decomposition of the thallium sulphostannate into thallium sulphide and soluble stannic sulphide, amounting to a loss of from two to three milligrams as stannic sulphide may take place on boiling as above, but on diluting the solution with water and allowing it to stand for two or three hours, stannic sulphide is again taken up and the precipitate finally consists of pure thallium sulphostannate. This precipitate is filtered in a Gooch crucible, is washed with water, dried at 105° , and weighed. Determinations of the thallium in pure fused thal- lous sulphate prepared as in the previous article gave 80.96, 80.97, 80.90, 80.96, 80.93, and 80.94 per cent. of thallium. Tl_2SO_4 —80.95 per cent. of thallium. The determination of thallium in 20 cc. portions of a thallic chloride solution gave by direct precipitation with sodium sulphostannate and primary sodium sulphide 0.9012 gram and 0.9010 gram Tl_4SnS_4 , while by precipitation after reducing with sulphur dioxide and boiling out the excess there was obtained 0.9011 gram and 0.9008 gram Tl_4SnS_4 .

Thalious Sulphide and Arsenic Trisulphide. Gunning² has described the precipitate formed between arsenious and thalious salts when treated with hydrogen sulphide in alkaline and in acid solutions. The composition of the precipitates varied widely with the methods of preparation and it was admitted that the substance did not seem to be a well defined chemical compound, yet the formula $TlAsS_2$ was given to it and it has gone into the literature as a compound of that composition. When such precipitates, obtained in either acid or alkaline solution, are examined under the microscope, they are found to be perfectly homogeneous for all compositions between pure arsenic trisulphide and about 62 mol. per cent. arsenic trisulphide. The color varies gradually from the light yellow of arsenic trisulphide through orange to a bright red as the amount of thalious sulphide increases. At about 62 molecular per cent. arsenic trisulphide, a second phase appears, the black thalious sulphide, and from that point to pure thalious sulphide two phases are present. These observations show that thalious sulphide and arsenic trisulphide under the conditions named form a limited series of solid solutions extending from pure arsenic trisulphide to about 62 molecular per cent. arsenic trisulphide

¹ Hawley, loc. cit.

² Chem. News, 17, 138 (1868); Arch. neerland. sci. exact. nat., 3, 86.

and that no compound is formed. From these precipitates acids will dissolve more or less thalious sulphide, depending on the concentration of the acid and the composition of the precipitate. Likewise solutions of alkaline sulphides will dissolve out varying amounts of arsenic trisulphide. The nearly constant composition of some of Gunning's precipitates obtained in acid solution with excess of thallium present was probably due to the nearly constant concentration of the acid used, realgar from Allchar, Macedonia. This mineral occurs in well formed crystals and is apparently a later formation than the realgar. One analysis

A mineral lorandite, has been described by Krenner¹ as occurring on a only is on record and this agrees with the formula $TlAsS_2$, but in view of the fact that a series of solid solutions extending on either side of that composition are known to exist, it is probable that other analyses would show different compositions. It is possible, of course, that under different conditions of formation, as with heat, pressure, or absence of water, a definite compound might be formed which did not exist under the conditions of preparation used above.

Thalious Sulphide and Arsenic Pentasulphide. When thallium salts and pentavalent arsenic salts are precipitated together by alkaline sulphides precipitates containing thalious sulphide and arsenic pentasulphide are obtained which vary in color and properties according to the composition. Microscopic examination of these precipitates showed the phases present. From pure arsenic pentasulphide to the composition corresponding to $3 Tl_2S.As_2S_5$ there were two phases distinguishable, the light yellow arsenic pentasulphide and a more crystalline orange colored phase. At the composition $3 Tl_2S.As_2S_5$ only the one orange colored phase was present but from that point to pure thalious sulphide the orange colored phase and the black thalious sulphide were present. These observations show that under the conditions given thalious sulphide and arsenic pentasulphide form a compound Tl_3As_4 but no solid solutions are formed. The same substances are formed by precipitation of thallium and arsenic salts with hydrogen sulphide in acid solution, but in this case it is difficult to prevent the partial reduction of the arsenic to the trivalent form and the consequent formation of the solid solutions, $xTl_2S.yAs_2S_3$.

On the other hand the solid solutions $xTl_2S.yAs_2S_3$ can be transformed into Tl_3As_4 , by treatment with sodium polysulphide. The compound Tl_3As_4 , thallium sulpharsenate, is an orange colored precipitate insoluble in dilute alkaline sulphides. On boiling with a concentrated solution of sodium sulphide it is partially decomposed, some arsenic pentasulphide going into solution and thalious sulphide remaining. Dilute acids decompose it with the evolution of hydrogen sulphide, thallium going into solu-

¹ Z. Kryst., 28, 97 (1895).

tion and arsenic pentasulphide remaining. When washed with water and dried it is perfectly stable in the air at ordinary temperatures, but it melts with slight decomposition at about 250° . This compound may also be used in the gravimetric determination of thallium in a manner similar to the thallium sulphostannate method.

Thalious Sulphide and Antimony Trisulphide; Thalious Sulphide and Antimony Pentasulphide. Thalious sulphide forms with both antimony trisulphide and antimony pentasulphide mixed precipitates similar to the solid solution $xTl_2SyAs_2S_3$. The two series of combinations, thalious sulphide with antimony trisulphide and thalious sulphide with antimony pentasulphide, are not readily distinguishable from each other by their physical properties and can be described in nearly the same words. The two entire series of compositions from pure thalious sulphide to pure antimony trisulphide or antimony pentasulphide are homogeneous, showing a complete series of solid solutions in each case. These solid solutions vary in color from black when high in thalious sulphide through red to orange when high in the antimony sulphide. Dilute acids readily dissolve some of the thalious sulphide, the solid solution becoming richer in the antimony sulphides and hence more resistant toward acids, so that only warm concentrated acids will completely remove the thallium sulphide. In the same way dilute alkaline sulphides partially dissolve the antimony sulphides but only hot concentrated alkaline sulphides will completely remove the antimony sulphides. These solid solutions are stable in the air except when high in thalious sulphide; then they are readily oxidized especially when not completely dry. Most of these solid solutions of intermediate composition if heated to about 100° in the air or even in the solution in which they are prepared sinter and become black and vitreous without change in composition.

Thalious Sulphide and Stannous Sulphide. Thalious sulphide and stannous sulphide form a complete series of solid solutions when precipitated together in acid or alkaline solutions. By starting with a solid phase high in thalious sulphide and gradually dissolving out the thalious sulphide with dilute sulphuric acid the whole series of compositions was obtained. Different compositions were also obtained by precipitating mixtures of stannous and thalious salts with colorless sodium sulphide. The precipitates obtained by either of these methods were found on microscopic examination to be entirely homogeneous. The color varied from black when rich in thalious sulphide through a light brown to a brownish black when high in stannous sulphide. Dilute acids extract part of the thalious sulphide, the solid becoming richer in stannous sulphide, and more resistant towards acids. Alkaline monosulphides are without

effect, but alkaline polysulphides change these solutions to thallium sulphostannate.

The Preparation of the Above Substances in Solutions Unsaturated with Hydrogen Sulphide. When any of the combinations of thalious sulphide mentioned in the preceding pages are prepared in solutions unsaturated with hydrogen sulphide, as, for instance, in ordinary sodium sulphide solutions, the solid cannot be filtered and washed without decomposition. This fact was mentioned by Gunning¹ in connection with the thalious-arsenious sulphide combinations when precipitated in alkaline solutions but he did not mention that if the alkaline solution is saturated with hydrogen sulphide the precipitate so prepared is stable on filtering and washing. The difference in the precipitates prepared in solutions saturated or unsaturated with hydrogen sulphide seems to be in the physical state only; the same compounds and the same solid solutions are formed and under the microscope the only difference is that the preparations in solutions saturated with hydrogen sulphide have a greater tendency toward crystalline structure and are not so finely divided. When once prepared in stable form the precipitates can be washed with ordinary sodium sulphide solution for some time without decomposition but finally the washings become turbid; such precipitates can however be washed with water for a very long time without any signs of decomposition. This is of especial importance in connection with the use of thallium sulphostannate in the gravimetric determination of thallium and shows the necessity of employing primary sodium sulphide in the precipitation.

Thalious Sulphide and Sulphur. Carstanjen² in his investigations on the compounds of thallium and sulphur obtained two compounds, Tl_2S and Tl_2S_3 , which he considered to be well characterized chemical individuals and a series of intermediate products which he described as homogeneous, crystalline substances of similar appearance. Although he expressly stated that these intermediate products might be of any composition between Tl_2S and Tl_2S_3 yet he gave two formulas, $3Tl_2S_3 \cdot 5Tl_2S$ and $Tl_2S \cdot Tl_2S_3$, which correspond to some of the analyses made and these formulas are given in the literature as representing definite compound Tl_2S with Tl_2S_3 . Schneider³ has also mentioned a compound $Tl_2S \cdot 2Tl_2S_3$ which he obtained while endeavoring to prepare a double sulphide of sodium and thallium by melting together thallium sulphate, sodium carbonate and sulphur and extracting the fused mass with water. The composition of this substance also will probably vary with the conditions of preparation. Strecker⁴ precipitated an am-

¹ loc. cit.

² J. pr. Chem., 102, 76 (1867).

³ Pogg. Ann., 151, 437; 153, 588 (1875).

⁴ Ann. chim. phys., 13, 1255 (1865).

moniacal solution of a thallic salt with hydrogen sulphide and obtained a brown precipitate which he considered to be Tl_2S_3 , but no analyses were made. Carstanjen¹ could obtain a product of the constant composition Tl_2S_5 only by melting thallium with a large excess of sulphur and distilling the excess of sulphur without access of air. Boettger² claimed to have prepared a still higher sulphide of thallium as a red precipitate insoluble in dilute acids by boiling a slightly acid thallium solution with excess of sodium thiosulphate. But Gunning³ showed that such a precipitate was formed in this manner only in the presence of arsenic, although he mentions that an instable red precipitate is formed by passing hydrogen sulphide into a solution of thallium which has been oxidized by aqua regia. Hofmann and Höchtlén⁴ prepared a higher sulphide of thallium by dropping thallic chloride into a 25 per cent. ammonium sulphide solution which had been saturated with sulphur. A heavy greenish precipitate was formed which on standing in the presence of the solution slowly became crystalline. These crystals were described as homogeneous, black, shining and opaque. Analyses gave Tl, 72.52 per cent., and S, 29.14 per cent. (calculated for Tl_2S_5 ; Tl, 71.83 per cent., S, 28.17 per cent.) and the substance was called the thallic salt of hydrogen pentasulphide. The papers cited above comprise the most important observations which have been published on the combinations of thallium and sulphur. The results obtained and the opinions expressed show the need of a systematic investigation of the whole field.

By means of two simple wet processes the whole range of concentrations between thallic sulphide on one end and pure sulphur on the other can be obtained. (1) By treating thallic sulphide with sodium sulphide solutions in which varying amounts of sulphur had been dissolved and which were then saturated with hydrogen sulphide combinations of thallium and sulphur containing from 90.49 per cent. $Tl(=Tl_2S)$ to about 70 per cent. Tl were obtained. In this method the sodium sulphide solutions must be kept saturated with either sulphur or hydrogen sulphide, otherwise the thallic sulphide will not take up sulphur from the solution. (2) By precipitating an acid solution of any thallium salt with a very slight excess of sodium polysulphide solution precipitates can be obtained which vary in composition from about 25 per cent. sulphur to nearly pure sulphur depending upon the acidity and concentration of the solution of the thallium salt and on the amount of polysulphide sulphur in the sodium polysulphide solution. Microscopic examination of the solids of different compositions obtained by these methods gave the follow-

¹ loc. cit.

² Ann. chim. phys., 128, 248 (1863).

³ loc. cit.

⁴ Ber. 36, 3090 (1903).

ing results. Between pure thallium sulphide and about 81 per cent. thallium the solid was entirely homogeneous; from 81 per cent. thallium to 76 per cent. thallium phases were distinguishable, while from 76 per cent. thallium to pure sulphur the solid was again homogeneous. These observations show that under the conditions of formation described above in the system thallium sulphide and sulphur there are two series of solid solutions, one extending from pure thallos sulphide to 81 per cent. thallium, the other from 76 per cent. thallium to pure sulphur. The first of these will be designated the α solid solution, the second one the β solid solution. The α solid solution when formed as above appears dark brown to the eye but when examined under the microscope it is of a light brown color; however, on pressing it firmly between the slide and the cover glass that part which comes in close contact with the cover glass appears entirely black. The general appearance seems to vary in different preparations made as nearly as possible under the same conditions and of the same composition, but, as is most important, the preparations are always homogeneous. When removed from the solution, washed with water and dried the tendency to oxidize and the ease of decomposition with acids decrease as the amount of sulphur increases. The end concentration of the α solid solution where the β solid solution began to appear could be determined only with an accuracy of about 0.3 per cent. thallium, within this limit of error the end concentration is 81 per cent. thallium. From the well defined series of trivalent salts of thallium and from the double sulphides of trivalent thallium with potassium sulphide as described by Schneider¹ and Schneider and Preiss² we would expect a definite compound Tl_2S_3 . The only safe conclusion to be drawn from these results obtained under one set of conditions is that under these conditions the end concentration of the α solid solutions happens to be near the composition Tl_2S_3 . But Carstanjan, as mentioned above, obtained the same end concentration when working under very different conditions, *i. e.*, at high temperatures and by dry process, from which it can be seen that the end concentration remains constant under diverse conditions. From all these considerations it may be concluded that the end concentration is 80.93 per cent. thallium ($=Tl_2S_3$) and that Tl_2S and Tl_2S_3 form a complete series of solid solutions. The β solid solution which begins to appear at about 81 per cent. thallium is so strikingly different from the α solid solution that it is very readily distinguished; the α solid solution is amorphous, brown and opaque, while the β solid solution is crystalline, red and translucent. The β crystals are mostly well formed, between crossed Nicols they show parallel extinction and they are apparently orthorhombic. When removed from the solution, washed with

¹ *loc. cit.*

² *Pogg. Ann.*, 138, 604 (1870).

water and dried they are entirely stable in the air showing no tendency to oxidize. They are much more resistant to the action of dilute acids than is the α solid solution, but alkalis and alkaline sulphides which are not sufficiently saturated with hydrogen sulphide or with sulphur readily decompose them by extracting sulphur. By the first method mentioned above, a solid with as low as 70.3 per cent. thallium can be obtained and for compositions with less thallium the second method must be used. The precipitates obtained by the second method are not well crystallized because their formation is so rapid, but in their color and other properties they resemble the more crystalline precipitates obtained by the other method. As the amount of thallium decreases the color becomes lighter and more of an orange tint, finally fading to the yellow of pure sulphur, while their stability in the presence of acids increases. When boiled with dilute acids the β solid solution gives up thallium sulphide, becoming richer in sulphur until finally the acid has no further effect. The only acid which will completely extract the thallium sulphide is fuming nitric acid and this acts only in consequence of its ability to oxidize some of the sulphur. Although thallos sulphide is practically insoluble in ordinary colorless alkaline sulphide solutions yet as more sulphur is dissolved in the solution and as more sulphur is in the solid in equilibrium with the solution the solid becomes more soluble until in solutions saturated with sulphur an appreciable amount of thallium can be found. On pouring slowly a dilute solution of any thallium salt into a warm solution of an alkaline sulphide saturated with sulphur at first a yellow precipitate forms but this dissolves on shaking. If as much thallium as will dissolve is added and the solution is allowed to cool, yellowish red crystals of the β solid solution separate out. These crystals contained not a trace of the alkalis used and there seems to be no tendency toward the formation of the double sulphides which were prepared in the dry way by Schneider¹. It is difficult to see why with the same general method of preparation Hofmann and Höchtlen obtained crystals which were black and opaque instead of red and translucent. If the thallium solution is added too rapidly and the precipitate is not given opportunity to reach equilibrium with the solution, part of the precipitate will appear black and opaque under the microscope, but on crushing these black lumps between the cover glass and the slide the smaller particles will transmit red light. By having an excess of alkaline polysulphide present and by allowing the mixture to stand in a warm place for several days with frequent shaking the whole solid can be obtained in well formed crystals which are red and translucent. The constancy of the composition of the sulphide obtained by Hofmann and Höchtlen was

¹ loc. cit.

due to the constant concentration of the sulphur in the ammonium polysulphide solutions used.

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THE VANADIUM SULPHIDE, PATRONITE, AND ITS MINERAL ASSOCIATES FROM MINASRAGRA, PERU.

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In the Engineering and Mining Journal, Sept. 1, 1906, p. 385, and in Informaciones y Memorias of the Society of Engineers of Lima, Peru, Vol. 8, pp. 171-185, 1906, are two accounts, by Foster Hewett and José J. Bravo, respectively, of a remarkable vanadium occurrence at Minasragra, about 46 kilometers from Cerro de Pasco in Peru, and 43 from the railway. The two accounts agree on all essential points that are common to both, though that of the Peruvian writer is much the more detailed as to the geography and geology of the region. The data immediately following are drawn from the publications referred to, and from additional information furnished by Mr. Hewett.

Cretaceous sedimentaries—shales, sandstones and limestones—dipping at about 45° have been intruded by two (Hewett) or three (Bravo) series of eruptive dykes, and at the point of greatest frequency of these intrusives occurs the vanadiferous deposit, which had as yet been opened up only very superficially by a few pits along an extension of 400 feet on the outcrop. The vanadiferous materials occur in vein formation and are three in kind, aside from alteration products that cover the surrounding surface. Under the hanging wall is a thickness of about eight feet of an amorphous material of complex mineral composition which will be designated hereinafter as the "ore." Its color is dark, almost black (dark green like olivenite, according to Hewett, bright lead gray with metallic luster on fresh surfaces but soon tarnishing, according to Bravo). Adjoining this material, without distinct line of demarkation beneath, is a singular, hard, coke-like carbonaceous matter, from eight inches to two feet in thickness, which blends on the farther side into a lustrous, black substance of from four to six feet thickness, designated as asphaltite by both the above-named writers, although it is a sulphur compound of carbon with very little hydrogen.

These three substances will now be considered in detail, beginning with the last, which, from its unique position among carbonaceous mineral substances, seems worthy of a specific name for the purpose of more ready separation from those bitumens and coals which it so strongly resembles in its superficial aspects. The name *quisqueite* is suggested by Mr. Hewett, after the settlement nearest to the locality of occurrence.