

XVI.—*On Thallium.*

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IN the present paper it is intended to collect together the various chemical and physical facts relating to thallium, accumulated during the few years which have elapsed since its discovery. The main body of the paper will be condensed from my own researches, already published in the *Philosophical Transactions*, the *Chemical News*, and elsewhere; it will also contain the results of many experiments which are now published for the first time; but I shall also freely make use of the researches of other chemists, where necessary, to fill up any gaps in the history of this metal. I shall follow the arrangement adopted in Gmelin's Handbook, and in cases where no authority is given for a statement, it may be accepted as resting upon my own experiments.

## LIST OF MEMOIRS RELATING TO THALLIUM.

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A. Lamy, *Verbal Communication on a Yellow Crystalline Substance*.—*Société impériale des Sciences de Lille*. May 2, 1862. — *Verbal Communication on a Metal supposed to be Thallium, obtained from the yellow crystalline substance*. *Société impériale des Sciences de Lille*. May 16, 1862.

W. Crookes, *Preliminary Researches on Thallium*.—Proceedings of the Royal Society, xii, 150 (June 19, 1862), and Chemical News, v, 349 (July 5, 1862).

A. Lamy, *On the Existence of a New Metal, Thallium*.—Comptes rendus, liv, 1255 (June 23, 1862).

F. Kuhlmann, *On some Compounds of Thallium with Organic Acids*.—Comptes rendus, lv, 607; Ann. Ch. Pharm. cxxvi, 75.

De la Provostaye, *On the Crystalline Form of some Salts of Thallium*.—Comptes rendus, lv, 610; Ann. Ch. Pharm. cxxvi, 79.

W. Crookes, *On the Discovery of Thallium*.—Cosmos xxi 628 (December 5, 1862).

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W. A. Miller, *Note on the Spectrum of Thallium*.—Proceedings of the Royal Society, xii, 407, and Chemical News, March 28, 1863.

M. Mascart, *Note on the Spectrum of Thallium*.—Comptes rendus, lvi, 139.

F. Kuhlmann, *On the Deposit in the Lead Chambers of Sulphuric Acid Works*.—Comptes rendus, lvi, 171 (Jan. 26, 1863).

W. Crookes, *On Thallium*.—Philosophical Transactions, Feb. 5, 1863.

W. B. Herapath, *On Thallium in Medicinal Preparations of Bismuth*.—Chemical News, Feb. 14, 1863.

W. Crookes, *Analytical Notes on Thallium—Separation of Thallium from Bismuth*.—Chemical News, March 7, 1863.

A. Matthiessen & C. Vogt, *On the Influence of Temperature on the Electric Conducting power of Thallium and Iron*.—Philosophical Transactions, March 12, 1863.

W. Crookes, *Analytical Notes on Thallium—Separation of Thallium from Copper*.—Chemical News, March 21, 1863.—*Separation of Thallium from Cadmium*.—Chemical News, March 28, 1863.

L. De La Rive, *On the Conducting Power of Thallium for Electricity*.—Comptes rendus, lvi, 588 (March 31, 1863).

W. Crookes, *On the Discovery of the Metal Thallium*.—Proceedings of the Royal Institution, March 27, 1863; and Chemical News, April 11, 1863.

A. Lamy, *On the Existence of a New Metal, Thallium*.—Ann. Ch. Phys., April, 1863.

Viktor von Lang, *On the Crystalline Form and Optical Properties of Sulphate of Thallium*.—Phil. Mag. [4] xxv, 248.

W. Crookes, *Analytical Notes on Thallium—On the Presence of Thallium in Commercial Hydrochloric Acid—Separation of Thallium from Iron*.—Chemical News, April 25, 1863.

W. T. Roepper, *On Thallium in Furnace products*.—Silliman's Journal, [2], xxxv, 420 (May, 1863).

W. Crookes, *Analytical Notes on Thallium—Separation of Thallium from Copper*.—Chemical News, May 9, 1863.

R. Böttger, *On the Extraction of Thallium from the Lead Chamber Deposit at the Sulphuric Acid Manufactory of Oker, and on some Compounds of this Metal*.—J. pr. Chem. xc. 22; Ann. Ch. Phys. cxxvi, 175.——*On the Extraction of Thallium from the Flue Dust of a Sulphuric Acid Manufactory*.—J. pr. Chem. xc. 30; Ann. Ch. Pharm. cxxvi 266

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J. Müller, *Determination of the Length of the Wave of the Green Thallium Line*.—Pogg. Ann. cxviii, 641; Phil Mag. [4], xxvi, 259.

W. Crookes and A. H. Church, *Contributions to the History of Thallium*.—Chemical News, July 4, 1863.

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E. Willm, *On the Estimation of Thallium by means of Permanganate of Potash*.—Bulletin de la Société Chimique de Paris, 1863, p. 352; Chemical News, August 29, 1863.

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R. Böttger, *On the Presence of Thallium in the Mineral Waters at Nauheim*.—Ann. Ch. Pharm. cxxvii, 368; J. pr. Chem. xc, 145.——*On a Simple Method of Extracting Thallium from Flue Dust*.—J. pr. Chem. xc. 151.

Erdmann, *On the Position of Thallium in the Classification of Metals*.—J. pr. Chem. lxxxix, 378.

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W. Crookes, *Contributions to the History of Thallium—Nitrate of Thallium. Perchlorate of Thallium*, Chemical News, October 24, 1863.——*Phosphate of Thallium*, Ibid, Nov. 7, 1863.——*Carbonate of Thallium*.—Ibid, November 14, 1863.——*Sulphate of Thallium*.—Ibid, November 21, 1863.——*Chromate of Thallium*.—Ibid, November 28, 1863.

Schrötter, *On the Presence of Thallium in Lepidolite and Mica*.—Wien. Akad. Ber., December 3, 1863.

W. Crookes, *Contributions to the History of Thallium—Acetate of Thallium*.—Chemical News, December 12, 1863.——*Oxalate of Thallium*.—Chemical News, January 2, 1864.

J. Nicklès, *Notes on the Spectral Ray of Thallium*.—Comptes rendus, lviii, 132; Chemical News, January 30, 1864.

J. Nicklès, *On an Iron and Thallium Alum*.—J. de Pharm. xlv, 24, 140.

Bischoff, *On the Presence of Thallium in Binoxide of Manganese*.—Ann. Ch. Pharm. cxxix, 375.

W. Crookes, *On the Solubility of some Thallium-salts*.—Chemical News, Jan. 23, 1864.——*On the Spectrum of Thallium*.—Ibid, January 30, 1864.

*History.*—Thallium was discovered in March, 1861, in a seleniferous deposit from the sulphuric acid manufactory at Tilkerode, in the Harz Mountains. In the distillation of some impure selenium prepared from this deposit, a considerable residue was left behind in the retort. This was at first thought to contain tellurium, until spectrum analysis showed me that a new element was present, whose spectrum consisted of a single, sharp, and brilliant green line. The element was at first suspected to be a metalloid, but further examination proved it to be a true metal. It was first obtained in a distinct metallic form by myself in September, 1861, and was afterwards exhibited in the International Exhibition, May 1, 1862, labelled "Thallium, a New Metallic Element." On the 16th of the same month, M. Lamy exhibited at the Imperial Society of Lille, a piece of metallic thallium, which was also deposited in the International Exhibition in June.

The name *thallium* is derived from the Greek word *θαλλός*, a green bud.

*Sources.*—As sulphide, thallium is a very widely distributed constituent of iron and copper pyrites. Upon examining a large collection of pyrites from different parts of the world, it was found present in more than one-eighth. It is not confined to any particular locality. Amongst those ores in which it occurs most abundantly (although in these cases it does not constitute more than from the 100,000th to the 4,000th bulk of the ore), may be mentioned iron pyrites from Theux near Spa in Belgium, from Namur, Philipville, Alais, the South of Spain, France, Ireland, Cornwall, Cumberland, and different parts of North and South America; in copper pyrites from Spain, as well as in crude sulphur prepared from this ore; in blende and calamine from Theux; in blende, calamine, metallic zinc, sulphide of cadmium, metallic cadmium, and cake sulphur from Nouvelle-Montagne; in native sulphur from Lipari and Spain; in bismuth, mercury, and antimony ores, as well as in the manufactured products from these minerals (frequently in so-called pure medicinal preparations of these metals); in commercial selenium and tellurium (probably as selenide and telluride).

Thallium is likewise frequently present in copper and commercial salts of this metal. In Spain a very impure copper is prepared in the following way:—Copper pyrites is allowed to oxidise in the air, and the resulting sulphate of copper is washed out; scrap iron is now placed in the liquid, which causes the

copper to precipitate in the powdery state. The metal is then collected together, dried, strongly compressed, and heated to the melting point. It is brought over to this country in the form of rectangular cakes, weighing about 20 lbs. each. The sulphide of thallium, oxidising to sulphate along with the sulphide of copper, is washed out by the water, and precipitated with the copper by the iron. The two metals readily alloy together.

Thallium is also present in tolerable quantity in lepidolite from Moravia, and in mica from Zinnwald (Schrötter). It has likewise been found in the deliquescent "Sel-à-Glace" from the mother-liquors of the salt-works at Nauheim. This consists of a mixture of the chlorides of magnesium, potassium, and sodium, with relatively considerable quantities of chlorides of rubidium and cesium, and sensible traces of chloride of thallium (Böttger). This mineral water is said by Böttger, to be the richest natural source of thallium. The quantity present is not stated but it is not likely to be richer than the Theux pyrites, which contains 1 in 4000.

Many samples of commercial sulphuric acid and yellow hydrochloric acid contain thallium. The source in these cases is evidently the pyrites used in the sulphuric acid works.

The optical process of detecting thallium in a mineral is very simple. A few grains only of the ore have to be crushed to a fine powder in an agate mortar, and a portion taken up on a moistened loop of platinum wire. Upon gradually introducing this into the outer edge of the flame of a Bunsen's gas-burner, the characteristic green line will appear as a continuous glow, lasting from a few seconds to half a minute or more, according to the richness of the specimen. By employing an opaque screen in the eye-piece of spectroscope to protect the eye from the glare of the sodium-line, I have, in half a grain of mineral, detected thallium when it was present only in the proportion of 1 to 500,000.

The sensitiveness of this spectrum reaction is so great that no estimate can be arrived at respecting the probable amount of thallium present. Before deciding whether a deposit or mineral contains sufficient of the metal to be worth extracting, it is necessary to make a rough analysis in the wet way by methods described in the next section.

*Preparation.* a. *From Iron pyrites.*—The pyrites from the Société Anonyme de Rocheux et d'Oneux, Theux, contains about 1 part of thallium in 4,000. Two tons of this ore, which I owe to the kindness of Professor Chandelon, were worked in the following manner:—

The pyrites, broken up into pieces of the size of a walnut, is distilled in hexagonal cast iron pipes, closed at one end, and arranged in a reverberatory furnace. Conical sheet-iron tubes are luted on to the open ends, and the retorts are kept at a bright red heat for about four hours. At the end of the operation, the receivers will be found to contain from 14 lbs. to 17 lbs. of dark green or grey-coloured sulphur for every 100 lbs. of ore used. The whole of the thallium originally in the pyrites will be found in this sulphur, from which it has now to be separated. The sulphur may be dissolved out by means of bisulphide of carbon, which leaves the sulphide of thallium behind; or it may be extracted by boiling with caustic soda. The former plan occasions less loss of thallium, but owing to the inconvenience of working with large bulks of bisulphide of carbon, I prefer the soda process. 12 lbs. of caustic soda, 18 lbs. of the thalliferous sulphur, and  $1\frac{1}{2}$  gallons of water are boiled together till the sulphur has dissolved; 6 gallons of water are added, and the clear liquid, when cool, is decanted from a voluminous black precipitate, which has been separated from the sulphur. The precipitate is then collected on a calico filter and washed. It contains the greater portion of the thallium in the form of sulphide, together with iron, copper, mercury, zinc, &c. Some thallium, however, remains dissolved in the alkaline liquid and is lost. The black precipitate is then dissolved in hot dilute sulphuric acid, to which a little nitric acid is added, and the liquid is diluted with water and filtered. Hydrochloric acid and sulphite of soda will now throw down the nearly insoluble, white, protochloride of thallium, which is to be filtered off and washed.

*b. From Sulphur or Pyrites in the wet way.* The material is dissolved in nitro-hydrochloric acid, until nothing but bright yellow sulphur is left; water is then added, and the filtrate is evaporated with sulphuric acid, until it is nearly dry, and sulphuric vapours are copiously evolved. The residue is dissolved in large excess of hot water, and carbonate of soda is added to alkaline reaction, and then cyanide of potassium (free from sulphide of potassium). The liquid is then heated gently for some time, and filtered. The precipitate contains the whole of the lead and bismuth which may be present, as carbonates, whilst the thallium is in solution. A current of sulphuretted hydrogen being now passed through the liquid, precipitates all the thallium, whilst the copper, antimony, tin, and arsenic remain dissolved. The precipitated sulphide is filtered off, washed, and dissolved in dilute

sulphuric acid, and the thallium is precipitated as chloride, by means of hydrochloric acid.

*c. From the flue-dust of Pyrites-burners.* This is by far the most economical source of thallium at present known. In burning thalliferous pyrites for the purpose of manufacturing sulphuric acid, the thallium oxidises along with the sulphur, and is driven off by the heat. If the passage leading from the burners to the leaden chambers is only a few feet long, the greater portion of the thallium escapes condensation, and volatilises into the leaden chambers; it there meets with aqueous vapour, sulphurous and sulphuric acids, and becomes converted into sulphate of the protoxide of thallium. This being readily soluble both in water and dilute sulphuric acid, and not being reduced by contact with the leaden sides, remains in solution and accompanies the sulphuric acid in its subsequent stages of concentration, &c. If, on the other hand, the passage connecting the burners and chambers is 10 or 15 (or more) feet in length, nearly the whole of the thallium is condensed, together with the multiplicity of other bodies which constitute "flue-dust." Accompanying the thallium, I have found mercury, copper, lead, tin, arsenic, antimony, iron, zinc, cadmium, bismuth, lime, and selenium, together with ammonia, sulphuric, nitric, and hydrochloric acids. The amount of thallium in these flue-deposits is very various. In many specimens it is not present at all, and in very few it amounts to as much as  $\frac{1}{4}$  per cent., although in some I have found as much as 8 per cent. of thallium. The plan I prefer for extracting the metal from the dust is the following which has been practically tested in Messrs. Hopkin and Williams' laboratory, on nearly 10 tons of material. The dust is first mixed in wooden tubs with an equal weight of boiling water, and is well stirred; during this operation a considerable quantity of nitrous acid is evolved; after which the mixture is allowed to rest for 24 hours for the undissolved residue to deposit. The liquid is then syphoned off, and the residue is washed, and afterwards treated with a fresh quantity of boiling water. The collected liquors, which have been syphoned off from the deposit, are allowed to cool, precipitated by the addition of a considerable excess of strong hydrochloric acid, and the precipitate, consisting of very impure chloride of thallium, is allowed to subside. The chloride obtained in this way is then well washed on a calico filter, and afterwards squeezed dry. Three tons of the dust have yielded as much as 68 pounds of this rough chloride.

The next step consists in treating the crude chloride in a platinum dish with an equal weight of strong sulphuric acid, and afterwards heating the mixture to expel the whole of the hydrochloric acid. To make sure of this, the heat must be continued until the greater part of the excess of sulphuric acid is volatilised. After this the mass of bisulphate of thallium is dissolved in about 20 times its weight of water, and the solution filtered. On the addition of hydrochloric acid to this solution, nearly pure chloride of thallium is thrown down; this is collected on a calico filter, well washed, and then squeezed dry. Lamy recommends that the highly acid flue-dust be previously calcined to get rid of the hydrochloric acid. This is useful when working on the small scale and with a limited supply of material, but the saving of thallium is so trifling, that it is not worth the extra trouble when working on many cwt. of dust.

*d. From the Saline Residues of the Salt-works at Nauheim.* Böttger adds an insufficient quantity of bichloride of platinum to the strong solution, and boils the precipitate 5 or 6 times with three times its weight of water. The insoluble residue consists of the platinum-salts of cæsum, rubidium, and thallium. Upon boiling these with a weak solution of potash and a little hyposulphite of soda, the solution soon becomes clear, whereupon cyanide of potassium and sulphuretted hydrogen are added. This precipitates the thallium as sulphide. The liquid is then to be filtered, the residue washed and dissolved in sulphuric acid, and the metal precipitated by metallic zinc.

*e. From Commercial Hydrochloric Acid.* Many samples of yellow hydrochloric acid contain thallium. It may be separated by neutralising with an alkali and adding sulphide of ammonium. The black precipitate contains the thallium, together with iron and some other metallic impurities of the acid. It is to be dissolved in sulphuric acid, and the thallium precipitated with hydrochloric acid as protochloride.

*Purification.* The crude protochloride of thallium obtained by either of the above methods is added by small portions at a time to half its weight of hot oil of vitriol in a porcelain or platinum dish, the mixture being constantly stirred and the heat continued till the whole of the hydrochloric acid and the greater portion of the excess of sulphuric acid are driven off. The fused bisulphate is now to be dissolved in an excess of water, and an abundant stream of sulphuretted hydrogen passed through the solution. The



precipitate, which may contain tin, arsenic, antimony, bismuth, lead, mercury, and silver, is separated by filtration, and the filtrate is boiled till all free hydrosulphuric acid is removed. The liquid is now to be rendered alkaline with ammonia, and boiled; the precipitate of iron and alumina, which generally appears in this place, is filtered off, and the clear solution evaporated to a small bulk. Sulphate of thallium will then separate out on cooling in the form of long, clear prismatic crystals. As sulphate of ammonia is much more soluble than sulphate of thallium, the latter can readily be separated from the small quantity of the former salt present. The two salts do not crystallise together.

In order to avoid the inconvenience of driving off the excess of oil of vitriol in the decomposition of chloride of thallium, it may in some cases be preferable to proceed as follows:—Boil the chloride of thallium in solution of sulphide of ammonium for five minutes: decomposition takes place readily. Filter and wash with hot sulphuretted water till no more chlorine can be detected in the filtrate, then dissolve the sulphide on the filter in dilute sulphuric acid, and treat the solution with ammonia, &c., as above directed.

In order to obtain the metal, sulphate of thallium is dissolved in twenty times its weight of water; the liquid is acidulated with sulphuric acid, and a current of electricity from two or three cells of Grove's batteries is passed through it, platinum terminals being used. The appearance presented when a tolerably strong solution of thallium is undergoing reduction is very beautiful. If the energy of the current bears a proper proportion to the strength and acidity of the liquid, no hydrogen is evolved at the negative electrode, but the metal grows from it in large crystalline fern-like branches, spreading out into brilliant metallic plates, and darting long needle-shaped crystals, sometimes upwards of an inch in length, towards the positive pole, the appearance strikingly resembling that known as the tin tree. Some of the tabular crystals, as seen in the liquid, are beautifully sharp and well defined, their angles appearing temptingly measurable; considerable difficulty is, however, met with in disengaging them from the electrode, and removing them in a perfect state from the liquid. So long as thallium is present in the solution, no hydrogen is evolved with a moderate current; as soon as bubbles of gas begin to form, the reduction may be considered complete. The crystalline metallic sponge may now be squeezed into a compact mass round the

platinum terminal, disconnected from the battery, quickly removed from the acid liquid, rinsed with a jet from a wash bottle, and transferred to a basin of pure water. The metal is then carefully removed from the platinum, and kneaded with the fingers into as solid a lump as possible. It coheres together readily by pressure, and will be found to retain its metallic lustre perfectly under water.

When considerable quantities of thallium are to be reduced to the metallic state, it is convenient to employ metallic zinc for the purpose. In the course of twenty-four hours, upwards of a quarter of a hundred weight of metal was reduced in the following way:—Plates of pure zinc (which should leave no residue whatever when dissolved in sulphuric acid) are arranged vertically round the sides of a deep porcelain dish holding a gallon. Crystallised sulphate of thallium, in quantities of about seven pounds at a time, is then placed in the dish, and water poured over to cover the salt. Heat is applied, and in the course of a few hours, the whole of the thallium will be reduced to the state of a metallic sponge, which readily separates from the plates of zinc on slight agitation. The liquid is poured off, the zincs removed, and the spongy thallium washed several times. It is then strongly compressed between the fingers, and preserved under water until it is ready for fusion.

The metal is readily obtained in the coherent form by fusing the sponge. This is most conveniently performed under cyanide of potassium on the small scale, and under coal gas when working with large quantities. In the former case the sponge, strongly compressed and quite dry, is broken into small pieces, which are dropped one by one into cyanide of potassium kept fused in a porcelain crucible. They instantly melt, forming a brilliant metallic button at the bottom. When cold, the cyanide of potassium may be dissolved in water, when the thallium will be left in the form of an irregular lump, owing to its remaining liquid and contracting after the cyanide has solidified.

On the large scale, the fusion is best effected in an iron crucible. This is placed over a gas-burner, and a tube is arranged so that a constant stream of coal-gas may flow into the upper part of the crucible. Lumps of the compressed sponge are then introduced, one after the other as they melt, until the crucible is full of metal. It is then stirred up with an iron rod, and the thallium may either be poured into water and obtained in a granulated form, or

cast into an ingot. Thirty or forty fusions have been performed in the same crucible without the iron being acted upon in the least by the melted thallium.

*Properties.* Thallium is a perfect metal with high metallic lustre. In colour it most resembles cadmium, not being so brilliantly white as silver, but free from the blue tinge of lead. The true colour can scarcely be seen by cutting or scraping the surface, as it tarnishes too quickly. It is best observed by scraping the metal under water, or by fusing it in hydrogen and allowing the melted globule to flow away from the dross. When fused under coal-gas, the liquid metal in the crucible can hardly be distinguished from mercury. It is susceptible of taking a very high polish by friction with appropriate materials, under water. Thallium tarnishes at ordinary temperatures, quickly becoming coated with a film, which almost entirely protects it from further action of the air. The specific gravity of thallium varies according to the treatment it has undergone. A lump melted and slowly cooled under cyanide of potassium was found to be as light as 11.81. After being strongly compressed it became 11.88. When *squeezed* into wire, a portion was found to be as high as 11.91. M. Lamy gives it as 11.86. M. De la Rive states it to be 11.85 after being melted, and 11.80 after being *drawn* into wire. It is the softest known metal admitting of free exposure to the atmosphere. The finger-nail, and even a piece of lead, scratch it readily. It marks paper like plumbago, forming a streak, grey at first, then turning yellow, and in a day or two fading nearly out. Sulphide of ammonium or sulphuretted hydrogen will at any time temporarily restore the dark streak. Thallium has less tenacity than lead, and does not become brittle at any temperature between 0°F. and its melting-point. It is very malleable, and can be hammered into foil as thin as tissue paper. When hammered it does not become sensibly harder. It can be drawn into wire only with difficulty, but it is squeezed into wire very readily by the process technically known as "squirting." Thallium wire is almost devoid of elasticity, retaining any form into which it is bent, with scarcely a tendency to spring to its original position. When first prepared the wire appears amorphous, and will remain so if kept at the ordinary temperature in carbonic acid or petroleum free from air. In water it gradually becomes crystalline, resembling the *moiré* of tin plate; this effect is immediately produced when thallium in wire, ingot, or plate, tarnished or clean, is boiled in water.

Thallium is a very crystalline metal, and crackles almost as much as tin when bent. When several pounds of the metal are fused and allowed to cool slowly, and the interior liquid portion poured off from that which has solidified, well-defined crystals in octahedrons and fern-like forms are produced. The melting-point of thallium is  $561^{\circ}$  F. (according to Lamy,  $554^{\circ}$  F.). In an experiment in which about two pounds of chemically pure metal were fused in an iron crucible, and the temperature taken by means of a thermometer specially made for this purpose by Mr. Casella, the mercury stood at  $561^{\circ}$  F. ( $293.9^{\circ}$  C.) during the whole of the time the thallium was solidifying. The bulb of the thermometer was perfectly covered by the melted metal, and it was kept constantly moving. Thallium does not become pasty; it expands considerably before complete fusion, and contracts strongly on cooling. Two pieces of the metal weld together under strong pressure at the ordinary temperature, and after filling a steel die with scraps and cuttings, they may be readily squeezed into a solid rod apparently as tenacious as when obtained by fusion.

Thallium, when heated in the air, begins to volatilise at a red heat, evolving brown vapours of oxide; it boils below a white heat, and may be distilled in a current of hydrogen. The hydrogen takes up mechanically a little thallium, which is not deposited upon traversing five feet of cold glass tubing, as the emergent gas, when ignited, burns with a bright green flame.

When heated to redness and plunged into oxygen, thallium burns brilliantly (Lamy). Before the blowpipe, on charcoal, the metal melts instantly, and evolves copious brown fumes. If the bead is heated to redness, it glows for some time after the source of heat is removed, continually evolving vapours which appear to be a mixture of metal and oxide. On cooling, the adjacent parts of the charcoal are found to be coated with small globules of volatilised metal, surrounded with a reddish amorphous sublimate of mixed proto- and peroxide. The principal globule of metal will also be coated with a fused layer of protoxide, resembling lead in this respect. When thallium is heated in an open glass tube, it melts and becomes rapidly converted into the more fusible protoxide, which strongly attacks the glass. This oxide is of a dark-red colour when hot, solidifying to a brown crystalline mass.

Some of the compounds of thallium are very volatile, the chlorides, for instance, distilling with the vapour of water, and

volatilising when heated to a temperature below redness. Other compounds, such as the sulphate and phosphate, will bear a full red heat without experiencing any loss. Thallium compounds are not, therefore, nearly so volatile as mercury-salts.

The most characteristic property of thallium is the intense green colour which the metal or any of its compounds communicates to a colourless flame. When examined in the spectroscope this colour is seen to be absolutely monochromatic, appearing as one intensely brilliant and sharp green line, coinciding with the number 1442·6 on the magnificent chart of the spectrum given by Kirchhoff, in the memoirs of the Berlin Academy for 1861. The thallium spectrum is simpler than that of any other element yet examined. An amplifying power as great as has ever been applied to the spectrum (16 heavy glass prisms), does not affect the integrity of the line, and the high temperature of the hydrogen or oxyhydrogen flame shows no new lines; thallium has therefore a simpler spectrum than sodium or lithium, which stand next to it in this respect.

The length of the wave of the green thallium line has been determined by Dr. J. Müller. He finds it to be 0·0005348 millimetre.

When sparks from an induction-coil are passed between two pieces of thallium wire, Dr. W. A. Miller finds that the light ceases to be purely monochromatic. When viewed by the spectro-scope, several new lines make their appearance; besides the usual intense line in the green, five others are particularly observable: first, a very faint one in the orange; next, two of nearly equal intensity in the green, more refrangible than  $Tl\ \alpha$ , with a third, much fainter, these three lines in the green being nearly equidistant; whilst, fifth, in the blue is a bright, well defined line. Dr. Miller has also examined the photographic spectrum of thallium; it contains several very characteristic groups of lines, recalling the features of the spectra of cadmium and zinc, and less strongly that of lead. For a detailed description the reader is referred to Dr. Miller's paper, quoted at the commencement.

The thallium line has no counterpart in the black lines of the solar spectrum.

The delicacy of the spectral reaction of thallium is very great. Experiments tried with solutions of definite strength show that the 5-millionth of a grain of sulphate of thallium is sufficient to produce the spectrum reaction.

Nicklès states that certain sodium-compounds possess an anta-

gonistic action to the green thallium line in the spectrum; that they possess a paralysing action on the thallium light, chloride of sodium especially having the property of obscuring the green ray. The experiments which he adduces in proof of this are by no means satisfactory, and several of his statements are decidedly erroneous. On the other hand, I have shown that when thallium is burnt in the presence of nearly a thousand times its weight of chloride of sodium, there is not the least interference between the two lines, which glow side by side, in total indifference as to each other's existence.

When a grain or two of metallic thallium is placed in a cup-shaped cavity in the lower carbon pole of an electric lamp, connected with 30 or 40 cells of a nitric acid battery, after making contact, the two poles can be separated for the space of an inch or more, voltaic connection being maintained by the bridge of thallium vapour rising from the cup. If projected on a screen, the arc is seen to emit absolutely homogeneous green light, and if passed through an appropriate arrangement of slit, prisms, and lenses, the green band of the spectrum will be projected of intense brilliancy, on a nearly black background.

Thallium is powerfully repelled by both poles of an electromagnet, nearly equalling bismuth in diamagnetic character.

The electric conductivity has been examined by Dr. Matthiessen and M. De la Rive. Taking silver as 100, the former experimentalist finds it to have a conducting power of 9.16, whilst De la Rive gives it as 8.64; in either case, it lies between tin and lead. Drs. Matthiessen and Vogt find that the conducting power of thallium decreases between  $0^{\circ}$  and  $100^{\circ}$  C., 31.420 per cent., which is a larger per centage decrement than that obtained for many other pure metals, namely, 29.307 per cent. The specific heat of thallium is given by Lamy at 0.0325, and by Regnault, at 0.03349 and 0.03361.

The atomic weight of thallium has been found by Lamy to be 204. My own determinations give, as the mean results of five experiments, 202.96. This subject is now under accurate investigation; the experiments are not yet completed, but as far as I am able to judge, they point to an atomic weight somewhat lower than the number I have given.

Thallium is easily reduced to the metallic state. When in aqueous solution, the metal is readily obtained by an electric current, or by the reducing action of metallic zinc. In the dry



state, its salts may be reduced by carbon and carbonate of soda at a high temperature, or from the chloride by an alkali-metal under the influence of heat. The pure metal is scarcely attacked by hydrochloric acid, even when boiling. It is dissolved somewhat more readily by sulphuric acid, especially if it be in contact with a piece of platinum; nitric acid attacks it violently.

In electro-chemical position, thallium is very near cadmium, being precipitated from the sulphate by zinc and iron, but not by cadmium, tin, or copper.

Several thallium-salts are sensitive to light; the protochloride darkens readily, although with by no means the rapidity of chloride of silver.

The position of thallium amongst elementary bodies has given rise to considerable discussion. On the continent it is generally classed amongst alkali-metals; in England it is, on the other hand, generally regarded as belonging to the silver and lead group. I give below the arguments which have been adduced on both sides.

In favour of the relationship of thallium to the alkali-metals, the following facts have been adduced:—It forms a readily soluble, highly alkaline oxide, a soluble and alkaline carbonate, an insoluble platinochloride, and with alumina, a double sulphate having the crystalline form of common alum, with a similar composition. Dumas also classes it with the alkali-metals, because it is necessary to halve its atomic weight in order to make its atomic heat equal the atomic heats of other metals; and he gives calculations to prove that the atomic weights of thallium and the alkali-metals are numerically related. Another argument on this side of the question is, that thallium sometimes accompanies the alkali-metals in mineral waters; this, however, is no argument at all, as the same reasoning would prove that iron and most other metals belong to the same class.

In support of the view that thallium is one of the heavy metals, the following reasons may be given:—The argument from the alkaline character of the oxide applies both ways. The oxides of lead, silver, and mercury, are well known to be soluble in water, and communicate to it an alkaline reaction. This is not very marked, owing to their slight solubility, but there is little doubt that if we could find a neutral liquid which would dissolve either of those oxides in larger quantities, their alkaline character would become

more apparent. Such a liquid, as Erdmann has pointed out, exists in a solution of neutral acetate of lead, which dissolves considerable quantities of oxide of lead, forming a solution as alkaline as that of oxide of thallium, and readily attracting carbonic acid from the air. Oxide of silver also appears to be more soluble in an aqueous solution of nitrate of silver than in pure water, and reacts more strongly alkaline. The slight affinity which oxide of thallium has for water, also shows it to be more allied to a heavy metallic oxide; it is not only non-deliquescent, but when its aqueous solution is evaporated even at the ordinary temperature over sulphuric acid in a vacuum, it gives up all its water and leaves the anhydrous oxide; it is difficult to conceive a more striking contrast to the behaviour of a true alkali under the same circumstances. The formation of an alum is considered by some authorities to be a strong argument in favour of the relationship of thallium to the alkali-metals. This argument falls to the ground now that Professor Church\* has obtained a silver-alum crystallizing in octahedrons, and containing 24 equivalents of water. The insolubility of the double chloride of platinum and thallium has, in my opinion, no bearing whatever on its classification. The metal stands alone in this respect; platinochloride of thallium is almost as insoluble as sulphate of baryta, and in comparison with this, the platinum-salt of potassium may be called extremely soluble; whilst even the rubidium and caesium salts must be regarded as soluble by the side of the thallium-salt. The fact of thallium having been obtained by Böttger, in conjunction with the alkalies in an analysis of a certain mineral water, is an accident, depending upon the special analytical process which he adopted.

Again, it is urged by Dr. W. A. Miller, that the chemical energy of the alkali-metals lithium, sodium, potassium, rubidium, and caesium, increases in the order mentioned, which is that of their equivalents; whilst thallium, with a higher equivalent than any of these, shows a greatly diminished chemical activity. Numerical relations between atomic weights are of little account, for figures can be made to prove anything. I may, however, remark that Dumas uses in his calculations an old and now admittedly erroneous equivalent for caesium (123 instead of 133), and that by similar processes of addition, multiplication, or sub-

\* Chemical News, March 26, 1864.



traction, it would be easy to prove that thallium belonged to any desired group especially the mercury, lead, and silver group.\*

As further reasons for classing thallium with the heavy metals, may be urged the complete, or nearly complete insolubility of its peroxide, sulphide, phosphide, iodide, bromide, chloride, chromate, and phosphate; its ready reduction from aqueous solutions of its salts by metallic zinc; the highly poisonous character of its compounds; the production of a brown insoluble peroxide by electrolytic means; its high atomic weight; the complexity of its photographic spectrum, shown by Dr. W. A. Miller, to contrast strongly with the simplicity of those of the alkali-metals; its low conducting power for electricity, which is close to that of lead and of tin, and much inferior to that of the alkali-metals; its specific heat which coincides with that of lead; its density and melting point, very near those of lead; and, finally, its physical appearance and characters, which approach so nearly to those of lead, that few persons would notice at first sight any difference between the two metals.

### *Compounds of Thallium.*

#### THALLIUM AND OXYGEN.

##### *A. Oxide of Thallium, TlO.*

Thallium oxidises in the air with almost the rapidity of an alkali-metal. When freshly cut with a knife, the proper colour of the metal may be seen, rapidly assuming a yellowish cast, which increases until the metallic lustre is obscured by a dark grey film resembling the superficial tarnish of cadmium. After the surface is coated with a film of oxide, scarcely any further change takes place, and the metal may be freely exposed to the air. If it is exposed to damp air containing carbonic acid, a white crystalline powder of carbonate of thallium appears on the surface. Perfectly bright metallic thallium has no taste; a tarnished surface, on the other hand, has a caustic alkaline taste, leaving a metallic flavour on the tongue for some hours afterwards. The superficial tarnish consists of the protoxide containing a minute quantity of the peroxide. If the metal has been oxidised by exposure

\*  $\text{Eq Hg} + \text{Eq Pb} = \text{Eq Tl}$ ;  $\text{Eq Ag} + 2\text{Eq Mb} = \text{Eq Tl}$ .

to the temperature of boiling water, rather more peroxide is formed, and when the heat is raised to the melting point of the metal, the protoxide which forms is mixed with a large quantity of peroxide. Thallium, when melted, behaves like lead, the oxide fusing like litharge; the fused oxide is absorbed by bone-ash, and a silver-thallium alloy can be cupelled like silver-lead. Thallium does not decompose pure water, either at the common temperature or when boiling; a piece of absolutely pure metal kept for nearly twelve months in a stoppered-bottle, under distilled water, had its metallic lustre undimmed; the sides of the glass were slightly turbid, and a few crystals of carbonate of thallium were apparent in the upper part of the vessel, the water reacting strongly alkaline. The oxygen was absorbed from the atmosphere. At a red heat the vapour of water is decomposed by thallium, with formation of oxide and separation of hydrogen, which burns with a green flame. Alcohol appears to be decomposed by the metal more readily than water.

The coating of tarnish forming on the surface of the metal is instantly removed by water. The oxide may be prepared by allowing granulated thallium to oxidise in warm moist air, and then boiling in distilled water. By repeating this operation two or three times, a saturated hot solution of the oxide is formed. Upon filtering, the small quantity of carbonate which may have formed separates at first in white needles, whilst, upon further cooling, the oxide crystallises out in yellow needles.

Anhydrous protoxide of thallium is formed by exposing these yellow crystals in a vacuum over sulphuric acid; it then forms a reddish-black mass, retaining the shape of the crystals. When heated to about the melting point of the metal, it melts to a brown limpid liquid, which, at a higher temperature, evolves reddish-brown vapours, partially oxidising at the same time to the peroxide. Upon cooling, the brown liquid solidifies to an almost black crystalline mass. The fused oxide attacks glass and porcelain, removing the silica. When heated, it always peroxidises slightly. Oxide of thallium is decomposed by hydrogen at a red heat, forming water and metallic thallium. The decomposition, however, is never perfect, owing to the oxide fusing and volatilising. When fused with sulphur, it forms sulphide of thallium, and in aqueous solution with metallic zinc, metal is precipitated, and oxide of zinc formed. When an electric current is passed through a solution of the oxide, it is also reduced to the metallic state.

*Combinations.* a. With water. a. HYDRATED OXIDE OF THALLIUM,

Hydrated oxide of thallium is prepared as above-described, or it may be obtained, as recommended by Lamy, by decomposing a solution of the sulphate with baryta-water, and evaporating the alkaline solution in a vacuum. This method is not so good as the one already described, owing to the large quantity of liquid required, and the great difficulty of getting the oxide free from baryta; it is, moreover, somewhat tedious. The best method of obtaining perfectly pure hydrated oxide of thallium, is to add water to the oily compound of oxide of thallium and alcohol. This at once separates the oxide in the form of a bright yellow crystalline mass, which may be separated from water and alcohol by exposure to warm dry air.

Hydrated oxide of thallium forms pale yellow, long, prismatic crystals, which lose water and become almost black and anhydrous by exposure to the temperature of a water-bath in air, or to sulphuric acid in a vacuum at the common temperature. On the addition of water, the dark oxide immediately becomes hydrated and yellow. It has a slight tendency to absorb oxygen, and after evaporation and re-solution, it always leaves a slight residue of peroxide.

β. AQUEOUS OXIDE OF THALLIUM. Protoxide of thallium is a powerful base, dissolving readily in water, and forming a colourless strongly alkaline solution. It has a slight odour, similar to that of potash, dissolves the skin, and feels greasy. It has a strong action on the hair and nails, staining them a deep and very permanent brown colour. It blues litmus paper, browns turmeric paper, has a metallic alkaline taste, and neutralises acids perfectly. It eliminates ammonia from chloride of ammonium, and reacts with hydrochloric acid, iodide of potassium, sulphide of ammonium, &c., in the characteristic manner of a thallium-salt. An aqueous solution of protoxide of thallium has a greater similarity to potash than to ammonia in its reactions with metallic salts. When added to solutions of salts of magnesium, cerium, manganese, zinc, cadmium, lead, iron (proto and sesqui), cobalt, nickel, copper, mercury, silver, and peroxide of thallium, it precipitates the respective oxides, without redissolving them in excess. From salts of aluminium and chromium it precipitates the hydrated oxides, and easily redissolves them when in excess, forming with alumina a solution unaltered by boiling, but precipitated by a current of

carbonic acid, and with chromium a green solution precipitated on boiling.

*b.* With acids it forms the THALLIUM-SALTS. The affinity of oxide of thallium for acids is considerable. The salts are for the most part colourless, unless the acid itself is coloured. They are mostly soluble in water, are neutral to test-paper, and have a slight metallic taste. They are strongly poisonous, three or four grains of the sulphate being sufficient to kill a small animal; the symptoms are somewhat similar to those produced by lead. After working with considerable quantities of sulphate, in the extraction of the metal from flue dust, the hands become burnt, and the epidermis cracks in all directions, looking yellow and horny. In this respect it somewhat resembles a mercury-salt. The salts when ignited, generally fuse at temperatures below redness, and then volatilise; some salts, such as the sulphate and phosphate, will stand a bright red heat without change. On charcoal before the blow-pipe, they volatilise, communicating an intense green colour to the flame. Their aqueous solution is rapidly precipitated in metallic crystals by *zinc*, and slowly by *iron*. *Phosphuretted hydrogen* precipitates a black phosphide. *Hydrosulphuric acid*, added to a solution of oxide of thallium combined with a weak acid, such as carbonic or acetic, separates the whole of the metal in the form of a deep brown sulphide; from solutions of thallium-salts of the stronger acids, such as sulphuric or nitric acid, sulphuretted hydrogen precipitates nothing if the acid is in excess, and only a small portion of the metal if the solution is neutral. *Sulphide of ammonium* precipitates thallium-salts completely, the precipitated sulphide being insoluble in sulphide of ammonium, in caustic alkalis, their carbonates and cyanides, and only slightly soluble in acetic acid. In salts of the protoxide, *hydrochloric acid* and *soluble chlorides* precipitate a difficultly soluble white chloride; *hydrobromic acid* and *bromides* precipitate a white, nearly insoluble bromide; and *hydriodic acid* and *iodides* precipitate an insoluble yellow iodide. *Alkalies, alkaline carbonates, or bicarbonates* produce no change in thallium proto-salts; *phosphate of soda* gives a white precipitate, nearly insoluble in ammonia, easily soluble in acids. *Chromate of potash* gives a yellow precipitate of chromate of thallium, insoluble in cold nitric or sulphuric acid, but turned orange-red on boiling in the acid solution. *Bichloride of platinum* precipitates a very pale yellow insoluble double salt.

B. *Peroxi*de of Thallium  $\text{TlO}_3$ .

Peroxide of thallium is always formed when metallic thallium is heated, or even when a solution of the protoxide is evaporated in the air. When the metal is burnt in oxygen, the product is chiefly peroxide. This compound is best prepared by adding potash, ammonia (or even protoxide of thallium) to a solution of sesquioxide or peroxide of thallium; in either case the peroxide is precipitated, and must be washed and dried at a temperature of  $500^\circ \text{F}$ . Peroxide of thallium is also formed when a voltaic current from two cells of Grove's batteries is passed through a solution of sulphate of thallium, platinum terminals being used. If the solution is perfectly neutral, thallium slowly makes its appearance at the negative pole, whilst the positive pole becomes coated with a film, presenting at first the most brilliant colours of thin plates, and gradually increasing in thickness until it becomes a cake of peroxide of thallium. As the sulphuric acid accumulates in the liquid, the peroxide at first formed gradually dissolves. If the solution of sulphate of thallium is rendered alkaline with ammonia, the peroxide is formed in larger quantity, scaling off and falling to the bottom of the liquid as soon as it becomes of a certain thickness. If the sulphate of thallium is acid, oxygen is evolved, and no peroxide is separated; in this case it dissolves in the acid present.

Anhydrous peroxide of thallium is a dark brown powder, fusing with difficulty and evolving oxygen at a red heat, becoming reduced to the protoxide. It is neutral to test paper, and insoluble in water. It dissolves readily in sulphuric, nitric, and hydrochloric acid, forming hygrometric and instable salts.

Hydrated peroxide of thallium,  $\text{TlO}_3 \cdot \text{HO}$ , is obtained by drying the precipitated peroxide at a temperature of  $212^\circ \text{F}$ .; it forms a brown powder, a shade lighter than the anhydrous oxide, and retains one equivalent of water. When formed in the wet way, it always appears to be hydrated. Reducing agents, such as sulphurous acid or oxalic acid, convert it to the lowest state of oxidation, forming sulphate or oxalate of the protoxide of thallium; in the latter case carbonic acid is evolved.

## THALLIUM AND HYDROGEN?

According to Dr. Herapath, when bismuth containing

thallium is tested with a hydrogen-flame by Marsh's method in a darkened room, a brilliant green light is produced where the flame impinges on a white porcelain plate. This experiment has not been confirmed, and I have been unable to obtain any evidence of the existence of a compound of thallium and hydrogen. When zinc is added to acid solutions containing thallium, the metal is reduced, but the evolved hydrogen contains no thallium; and the same result is obtained when an alloy of thallium and zinc is dissolved in sulphuric acid. When hydrogen is passed over metallic thallium at a red heat, the metal volatilises, and is mechanically carried forward by the current of gas, communicating to the flame a brilliant green colour. The thallium, however, does not appear to be chemically united to the hydrogen, as it is gradually deposited as a dark powder upon the cold sides of the glass tube, although the flame still burns green after the gas has passed through six feet of cold tubing. This hydrogen flame burns with a bright green colour, and deposits a reddish brown mirror with a metallic lustre, upon a cold porcelain surface. This mirror has many points of resemblance to the one given by arsenic. Upon moistening it with sulphide of ammonium, it becomes rather darker in colour, but is not otherwise affected. An aqueous solution of chloride of lime dissolves the mirror readily. Upon exposing the deposit to the vapour of iodine, it turns permanently yellow, and, upon subsequent addition of sulphide of ammonium to the yellow iodide, the latter becomes of a dark, reddish brown colour, but does not dissolve. Upon strongly heating the glass tube through which the hydrogen containing thallium is passed, no metallic deposit is formed on the glass. The two former characters serve to distinguish the thallium mirror from antimony, whilst the two latter distinguish it from arsenic.

#### THALLIUM AND CARBON.

*Carbonate of Thallium*,  $\text{TlO.CO}_2$ .—The film of oxide which forms upon the surface of metallic thallium when exposed to the air, gradually absorbs carbonic acid and becomes converted into carbonate, which frequently appears in the form of crystalline needles. A saturated aqueous solution of oxide of thallium absorbs carbonic acid rapidly and deposits carbonate of thallium in crystals. Carbonate of thallium may be prepared in quantity by allowing granulated

thallium, slightly moistened with water, to oxidise in a warm atmosphere. Upon boiling out with water containing an excess of carbonate of ammonia, and filtering, crystals of carbonate of thallium will be deposited as the solution cools. The first crop of crystals generally have a slight yellow tinge, owing to the presence of a trace of oxide or peroxide. Recrystallisation will render them perfectly white. Carbonate of thallium crystallises in long prismatic needles; they are perfectly white, have a brilliant appearance, are highly refractive and very heavy, resembling a salt of lead. The salt is anhydrous; its taste is mildly caustic and somewhat metallic, remaining on the tongue for a considerable time. When heated, it fuses much below redness to a clear liquid which solidifies to a dark grey crystalline mass. It may be kept fused for a considerable time without decomposition or loss of weight, but when heated to dull redness, it evolves white vapours, and bubbles of gas make their appearance. The specific gravity of the fused salt is 7.06 (Lamy). It is not very soluble in cold water; 100 parts of water at 60° F. only dissolve 4.02 parts; at 140° F. the same quantity of water dissolves 11.7 parts, and at the boiling point water dissolves 27.21 parts. The specific gravity of a cold saturated solution is 1.037. M. Erdmann has said that carbonate of thallium has no alkaline reaction; to test this, a warm saturated solution of pure carbonate of thallium had a rapid stream of carbonic acid passed through it, until the liquid was quite cold and the excess of salt had crystallised out. Even then the solution was alkaline, both to turmeric and litmus paper, although the liquid contained an excess of carbonic acid gas, which was liberated from all parts when gentle heat was applied. Carbonate of thallium therefore is not only alkaline, but an excess of carbonic acid will not render it neutral. The crystals deposited from this carbonic acid solution were analysed by being dried over sulphuric acid in a vacuum. They lost no weight when heated to the melting point. The carbonic acid was determined in the usual manner, and the thallium by precipitation with platinum. The numbers agreed closely with the formula  $\text{TlO.CO}_2$ . Crystals of carbonate deposited from a solution containing an excess of carbonate of ammonia were found to have the same composition.

#### THALLIUM AND BORON.

*Borate of Thallium.*—Boracic acid added to a solution of car-



bonate of thallium, or borax added to sulphate of thallium, precipitates a white granular borate of thallium, insoluble in excess of the precipitant and in cold dilute sulphuric acid; soluble in boiling water.

### THALLIUM AND PHOSPHORUS.

A. *Phosphide of Thallium.* Phosphuretted hydrogen passed through an ammoniacal solution of sulphate of thallium precipitates phosphide of thallium as a black insoluble powder, permanent in the air at common temperatures.

B. *Phosphate of Thallium.* A hot solution of nitrate of thallium is heated nearly to the boiling point, and glacial phosphoric acid added to it; upon neutralising with ammonia, a thick felt-like mass of crystals of phosphate of thallium is deposited. This salt is soluble in nitric acid, separating in large crystals. Lamy describes the phosphate as a soluble salt, like the carbonate; but experiment shows that 100 parts of water at 60° F. dissolve only 0.497 parts, and the same quantity of boiling water dissolves 0.6712 parts. The salt, dried over sulphuric acid in a vacuum, loses nothing but a minute trace of hygroscopic water, upon being heated to full redness for two hours in an open crucible. It melts below redness, forming a deep brown very mobile liquid, becoming as it cools dark orange yellow, then pale yellow, and, finally, solidifying to a highly crystal-white mass. The composition of the salt is most probably  $3\text{TlO} \cdot \text{PO}_5$ , it cannot contain either water or ammonia, as it loses nothing at a red heat; on boiling it with nitrate of silver, the characteristic yellow phosphate of silver  $3\text{AgO} \cdot \text{PO}_5$  is instantly produced, the solution remaining neutral.

### THALLIUM AND SULPHUR.

A. *Sulphide of Thallium*,  $\text{TlS}$ .—From neutral solutions of nitrate, sulphate or chloride of thallium, sulphuretted hydrogen precipitates only a small portion of the metal, as a grey-black sulphide. If other metals are present which are completely precipitated by this gas, they carry down larger quantities of thallium. Solutions of acetate, oxalate, or carbonate of thallium are completely precipitated. Sulphide of ammonium precipitates all thallium-salts, forming a brownish black, dense, flocculent precipitate; if present in small quantities only, the minute



particles of sulphide suspended in the liquid quickly collect together into a few large clots at the bottom of the vessel, leaving the solution quite clear. Sulphate of thallium projected into fused cyanide of potassium is reduced to the state of sulphide, forming in this case a brittle metallic-looking mass, of the lustre of plumbago, and fusing more readily than the metal. When precipitated in the wet way, the sulphide oxidises in the air, and whilst being washed, unless the washing-water contains a little sulphide of ammonium, a considerable quantity of the precipitate will be converted into sulphate of thallium, which passes through into the filtrate. After drying in hydrogen, it still oxidises on exposure to the air. According to M. Lamy, its specific gravity is 8. The higher compounds of thallium appear to be reduced to the state of protosulphide by ebullition with an excess of sulphide of ammonium. Precipitated sulphide of thallium is readily soluble in dilute sulphuric or nitric acid, and is insoluble in sulphide of ammonium or cyanide of potassium. Analysis shows that the composition is  $\text{Tl}_2\text{S}$ , but the numbers did not agree within 0.5 per cent., owing to the difficulty of weighing sulphide of thallium without oxidation.

**B. Hyposulphite of Thallium.** When sulphate of thallium is added to hyposulphite of soda, a white curdy precipitate falls. This is soluble in boiling water, and separates in rhombic crystals on cooling. When it is boiled in a solution containing a slight excess of sulphate of thallium, a somewhat larger crystalline deposit is produced. When heated with an excess of hyposulphite of soda, it dissolves, with partial decomposition and production of brown flocks, but deposits no crystals on cooling. It is not soluble to any extent in a cold solution of hyposulphite of soda.

**C. Sulphate of Thallium.**—*a. Monobasic,  $\text{TlO} \cdot \text{SO}_3$ .* Formed by dissolving thallium in dilute sulphuric acid. Hydrogen is evolved, and upon evaporation, the solution deposits crystals of the sulphate. It forms long, thin tabular crystals (right rhombic prisms, Lamy), very brilliant and colourless. Exposed to a dull red heat, they decrepitate slightly without fusing. At a bright red heat, they melt to a clear liquid, which, at a somewhat lower temperature, solidifies to a dirty yellow crystalline mass, gradually becoming lighter yellow, and finally, when cold, quite white. The total loss in an experiment in which the sulphate was kept at bright redness for eight hours was only 0.3 per cent., most of which went off at the first heating. The specific gravity of fused sulphate of thallium is

6.77 (Lamy). It dissolves in 21.1 times its weight of water at 60° F., and in 5.4 parts of boiling water, forming a neutral solution. The crystals contain no water of crystallisation; and upon analysis give numbers closely agreeing with the formula  $\text{TlO} \cdot \text{SO}_3$ . The composition of the salt was found to be the same, whether it was crystallised from a slightly acid solution, or from an ammoniacal solution containing sulphate of ammonia. When sulphate of thallium is heated in a crucible with black flux or with cyanide of potassium, it is first reduced to the state of sulphide, and then to the metallic state. It is difficult, however, to remove all the sulphur in this way.

*b. Acid Sulphate.* When sulphate of thallium is heated with one atom of oil of vitriol, or when the chloride is decomposed with an excess of sulphuric acid, a bisulphate is formed, which is more fusible than the neutral sulphate, and at a red heat gives off anhydrous sulphuric acid, leaving the compound *a*.

*D. Sulphate of the Teroxide.* When teroxide of thallium  $\text{TlO}_3$ , is dissolved to saturation in slightly warm dilute sulphuric acid, and the solution is evaporated, a granular crystalline deposit of sulphate of teroxide of thallium is produced. This is very soluble in water containing a trace of free sulphuric acid, but when dissolved in pure water, it decomposes, with deposition of teroxide of thallium. When heated to redness, it melts, becomes yellowish, loses oxygen and sulphuric acid, and finally leaves a residue of ordinary sulphate of thallium.

#### THALLIUM AND SELENIUM.

*Selenide of Thallium* is formed by fusing together equal equivalents of the two elements. It is very fusible, and of a greyish black colour (Lamy).

#### THALLIUM AND IODINE.

*Iodide of Thallium*,  $\text{TlI}$ .—When the two elements are heated together, they combine, without evolution of light, and form the proto-iodide. The same compound is readily formed by double decomposition, between an alkaline iodide and a salt of the protoxide of thallium. It forms a beautiful yellow powder, rather darker than sulphur, fusible below redness, and yields a scarlet liquid, which, as the mass cools, remains scarlet for some time after it has solidified, and then suddenly changes to bright yellow.

When the precipitated and dried iodide of thallium is spread on paper with a little gum-water, it undergoes a similar, but opposite change to that experienced by iodide of mercury, upon application of heat. The yellow surface, when held over a spirit-flame, suddenly becomes scarlet, and will frequently remain so, after cooling, for several days. Hard friction with a glass rod changes the scarlet colour back to yellow. Iodide of thallium is very difficultly soluble in water, requiring 4453 parts of water at 63° F., or 842.4 parts of boiling water to dissolve it; it is slightly more soluble in an aqueous solution of iodide of potassium.

#### THALLIUM AND BROMINE.

*Bromide of Thallium* is formed by adding thallium to bromine, the two bodies then combining, with evolution of heat. It is also produced by double decomposition. It forms a very pale yellow precipitate, fusible below redness. It is intermediate in solubility between the iodide and chloride.

#### THALLIUM AND CHLORINE.

A. *Protochloride of Thallium*,  $\text{TlCl}$ .—Metallic thallium is attacked at the ordinary temperature by chlorine; when heated in the gas, it burns and forms a yellow liquid, which solidifies on cooling to a pale yellow or white crystalline mass. If excess of chlorine has been present, the product consists almost entirely of higher chlorides, but in presence of an excess of thallium, the white protochloride is the only compound formed. Boiling hydrochloric acid attacks thallium but slowly, the action soon ceasing, owing to the formation of a layer of difficultly soluble chloride of thallium. When hydrochloric acid, or a soluble chloride, is added to a solution of the protoxide of thallium or one of its soluble salts, a white curdy precipitate of protochloride of thallium is thrown down, scarcely to be distinguished at first sight from chloride of silver. When boiled in water, it dissolves like chloride of lead, and separates again on cooling; the crystals, however, are much smaller and less brilliant than those of chloride of lead. One part of the chloride dissolves in 283.4 parts of water at 60° F., and in 52.5 parts of boiling water. It is insoluble in alcohol, and scarcely, if at all, more soluble in aqueous ammonia, cyanide of potassium, or hydrochloric acid, than it is in water. When boiled in nitric acid or aqua regia, it is converted into a higher chloride.

It may be heated to a temperature of 500° F., without loss of weight; at a slight increase of heat, it suddenly melts to a thin brown liquid, white vapours being simultaneously evolved. On cooling, it solidifies to a white crystalline mass, somewhat resembling horn-silver, possessing a brilliant lustre, but being only slightly flexible. The specific gravity of the fused chloride is 7·02 (Lamy). The fused lump is reduced to the metallic state by zinc and dilute acid, like fused chloride of silver. According to Lamy, chloride of thallium is unalterable by light; experiment, however, shows that it undergoes a considerable darkening when exposed either to sunlight or diffused daylight. Protochloride of thallium is also precipitated when sulphurous acid, or an alkaline sulphite, is added to one of the higher chlorides of thallium.

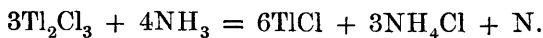
B. *Sesquichloride of Thallium*.— $\text{Tl}_2\text{Cl}_3$ . This compound is prepared by dissolving the metal or the protochloride in nitro-hydrochloric acid. On cooling it separates in yellow crystalline scales. It may also be prepared by heating the terchloride till it fuses, and no more chlorine is evolved. When heated it melts below redness, forming a dark brown liquid, which solidifies to a lighter coloured mass. Sesquichloride of thallium is soluble in 380·1 times its weight of water at 60° F., and in 52·9 parts of boiling water. Pure water produces a slight decomposition into teroxide and protochloride, which, however, may be prevented by the addition of a drop of nitric or hydrochloric acid. When slowly crystallised from slightly acidulated boiling water, it separates in brilliant orange-yellow hexagonal plates, considerably darker than when it is obtained by more rapid crystallisation, and presenting the closest resemblance to iodide of lead. Sesquichloride of thallium is also precipitated by the cautious addition of sulphite of soda to one of the higher chlorides. Whenever it separates from a liquid, it shows remarkable crystalline characters, and when just precipitated, it produces a magnificent satiny lustre in the liquid. Ammonia, potash, or even a solution of oxide of thallium, added to the sesquichloride, produces instant decomposition into teroxide and protochloride, according to the following equation :



When pure dry ammoniacal gas is passed over the sesquichloride, heat being applied with a spirit-lamp, the salt first assumes a deep orange tint, without fusing, and loses its brilliant, almost metallic lustre. On increasing the heat, the chloride fuses,

and at the same time chloride of ammonium vapours are abundantly evolved. The melted compound froths up, and assumes a deeper tint, ultimately becoming brown, and then gradually paler, until there finally remains perfectly white protochloride of thallium.

The reaction between ammonia and sesquichloride of thallium is represented by the following equation :—



C. *Bichloride of Thallium* is formed by carefully treating either thallium or the protochloride in a slow current of chlorine, the resulting chloride being kept liquid. This bichloride is pale yellow, rather hygrometric, and decidedly more fusible than the sesquichloride. It is reduced by heat to the sesquichloride (Lamy).

D. *Terchloride of Thallium*.—The terchloride is formed by dissolving the teroxide in hydrochloric acid, or by acting upon thallium or a lower chloride, with a large excess of chlorine, at a gentle heat. It is white, crystalline, and deliquescent, melting with the greatest facility, and almost immediately decomposing, with loss of chlorine (Lamy). It is converted by heat into the sesquichloride.

E. *Chlorate of Thallium*.— $\text{TlO.ClO}_3$ . This salt may be prepared by dissolving the metal in chloric acid, a very gentle heat being employed, or by mixing together saturated aqueous solutions of chlorate of potash and nitrate or acetate of thallium. It forms a beautiful difficultly soluble salt, crystallising in long needles; it is anhydrous, easily fusible, and readily decomposed by heat.

When the chlorate is heated with an excess of chloric acid, the crystals dissolve; the liquid turns yellow; oxygen-compounds of chlorine are evolved; and when the solution is evaporated to a syrupy consistence, small brilliant colourless crystals are deposited, which are instantly decomposed when water, alcohol, or ammonia is added, with production of the brown teroxide of thallium. The salt is remarkable for its immediate decomposition in the presence of water. If the colourless crystals are allowed to remain for a minute exposed to the ordinary atmosphere, they turn dark and blacken instantly when breathed upon, evolving a strong chlorous odour. A drop of water placed on the filtering paper in which the crystals have been dried, instantly blackens it. I have not satisfactorily determined the composition of these

crystals. When decomposed by ammonia, they yield 71.47 p. c. of hydrated teroxide of thallium, only very minute traces of thallium and hydrochloric acid being found in the filtrate. On first describing this salt, I assumed that it consisted of perchlorate of thallium with three atoms of water, and was resolved into hydrated teroxide of thallium, chloric acid, and two atoms of water. This would yield 71.62 per cent. of hydrated teroxide of thallium; but the same analytical result would be obtained on the assumption that the formula of the crystals was  $\text{TlO}_3.\text{ClO}_5.3\text{Aq}$ . This subject is now under further examination.

#### THALLIUM AND NITROGEN.

Attempts have been made to prepare a nitride of thallium, but hitherto without success.

*Nitrate of Thallium.*  $\text{TlO.NO}_5$ .—Cold concentrated nitric acid scarcely affects thallium at all, but when diluted with its own bulk of water or warmed, it is acted upon violently, with evolution of nitric and nitrous oxide. No ammonia is produced in the reaction. As the liquid cools, an abundant crystallisation of nitrate of thallium takes place. The great bulk of this is nitrate of the protoxide, but it contains a small quantity of a persalt of thallium, which is not entirely removed by recrystallisation. It may be detected by adding a few drops of ammonia to the solution of the nitrate; a slight precipitate of hydrated teroxide of thallium will be produced, scarcely to be distinguished in appearance or colour from sesquioxide of iron. This impurity may be entirely removed by fusion. When the white crystals of nitrate of thallium are heated to a temperature of about  $400^\circ \text{F}$ ., they melt to a clear liquid, a considerable amount of froth at first covering the surface, and gradually disappearing, until the liquid is quite clear, with the exception of a brown powder, consisting of teroxide of thallium, suspended in it. After cooling, the salt is perfectly soluble in water, with the exception of this brown powder, and the filtered solution deposits on evaporation brilliantly white crystals of pure nitrate of thallium.

The crystals when heated to a temperature of  $394^\circ \text{F}$ ., melt to a liquid as clear and colourless as water. Fifty grains have been kept at a temperature of about  $500^\circ \text{F}$ . for six hours without appreciably losing weight. Upon cooling, the fused salt solidifies to a white opaque crystalline mass. Nitrate of thallium is soluble

in 9.4 times its weight of water at 60° F., and in considerably less than its own bulk of boiling water, forming a syrupy solution. (Lamy states that 100 parts of boiling water dissolve 580 parts of the salt.) It separates on cooling in white prismatic needles, which are anhydrous and are insoluble in absolute alcohol. Its aqueous solution is neutral to test-paper.

#### THALLIUM AND ALUMINIUM.

*Double Sulphate of Alumina and Thallium.*—*Thallium-alum.*—When equivalent quantities of sulphate of thallium and sulphate of alumina are mixed together and the solution is evaporated, brilliant and colourless crystals of thallium-alum are produced in large octahedra. These are identical in crystalline form with potash-alum (Lamy).

#### THALLIUM AND CHROMIUM.

A. *Neutral Chromate of Thallium.*—When yellow chromate of potash is added to a neutral salt of the protoxide of thallium, and the mixture rendered slightly alkaline with ammonia, a pale-yellow precipitate is produced, very difficultly soluble in water, and yielding on analysis numbers which agree with the formula  $\text{TlO} \cdot \text{CrO}_3$ .

B. *Bichromate of Thallium.*—On adding bichromate of potash to a neutral salt of protoxide of thallium, an orange-yellow precipitate is produced, which has the formula of bichromate of thallium.

C. *Terchromate of Thallium.*—Either of the above compounds, boiled with nitric acid, is converted into a brilliant orange-red compound, which, on analysis, gives results pointing to the formula of a terchromate. If the nitric acid be moderately strong and in large excess, either of the chromates is dissolved, and the solution, on cooling, deposits magnificent cinnabar-red crystals, which appear to be the compound C. This salt is one of the most insoluble of the compounds of thallium, requiring 2814 parts of cold water, and 438.7 parts of boiling water, to dissolve it. Sulphuric acid acts like nitric acid. Hydrochloric acid dissolves the chromates readily, chlorine being evolved, and a soluble perchloride being produced.

When mixed with hydrochloric acid and alcohol, or with sulphite of soda, these compounds are quickly decomposed, protochloride of



thallium being precipitated, whilst sesquichloride of chromium remains in solution. The former compound, being insoluble in alcohol, affords an easy means of analysis.

#### THALLIUM AND MANGANESE.

These elements occur together in nature. Three years ago, before I had published anything respecting thallium, my friend Mr. C. Greville Williams, to whom I had sent a small portion of substance which showed the green line, wrote to me, in a letter dated March 10th, 1861, "I have a minute blowpipe specimen of pyrolusite, which gives your green line as distinctly as the residue sent by you. I enclose half my specimen." In consequence of this, an immense number of specimens of pyrolusite and similar minerals were examined, but as no other specimens were found to give the green line, the matter was allowed to drop. The above observation has now met with confirmation. Professor Bischoff, in a note to the number of the *Annalen der Chemie und der Pharmacie*, for March, 1864, announces the occurrence of thallium in a specimen of binoxide of manganese, but, like Mr. Williams, he has not succeeded in obtaining more than a small quantity of this mineral.

When manganese and thallium occur together in solution, the thallium may be separated by precipitation with iodide of potassium, sulphurous acid having previously been added to reduce the metals to the state of proto-salts.

#### THALLIUM AND BISMUTH.

These elements frequently occur together in minerals containing bismuth, and thallium may frequently be detected in medicinal preparations of bismuth, especially the carbonate. Dr. W. Bird Herapath says that when a solution of bismuth containing thallium is introduced into a hydrogen apparatus, the resulting gas will contain a volatile thalliuretted hydrogen, which burns with a green flame. I have already referred to this subject in a previous part of this paper, and have been quite unable to detect thallium in bismuth by this means. There are very delicate analytical processes for detecting thallium in bismuth. The bismuth-salt is to be first obtained in the form of a dilute solution, any convenient acid being used for this purpose. A slight excess of carbonate of soda is now added, and then a little cyanide of potassium free from sulphide. The mixture is to be



gently warmed, and allowed to stand for ten minutes, then filtered, and a few drops of sulphide of ammonium added to the clear liquid. If the slightest trace of thallium were originally present in the bismuth-compound, it will now be precipitated as a sulphide, which, upon gently heating the liquid (not to the boiling-point), gradually collects together in deep brown, almost black flakes, after the characteristic manner of sulphide of thallium.

This process is one of extreme delicacy; by means of it one part of thallium can be detected in the presence of more than 100,000 parts of bismuth. In some cases, the thallium is present in so small a quantity as to occasion only a slight darkening of the liquid when the sulphide of ammonium is added. Upon allowing this to digest at a gentle heat, it will generally collect in the form of a few flakes at the bottom. These may be collected together on a small filter, washed to the apex, and tested in the spectroscope. When the precipitate is only present in sufficient quantity to produce a faint dark stain on the filter-paper, the latter may be partially dried by pressure between blotting-paper, opened, and the stained surface scraped up with a knife. The dark fibres are now to be twisted up in a platinum wire loop, and held in the flame of the spectroscope, when they will give abundant indications of the presence of thallium.

#### THALLIUM AND ZINC.

I have met with many specimens of blende and calamine, especially from Nouvelle Montagne and the neighbourhood of Spa, in Belgium, in which thallium was present in tolerable quantity. In such cases it accompanies the zinc in most of its preparations, and may, therefore, be frequently detected in the commercial metal. By proceeding in the following manner, the black residue which is left behind when zinc is dissolved in sulphuric acid will generally be found to contain thallium. The residue is dissolved in nitric acid; the solution evaporated with excess of sulphuric acid; the residue dissolved in a small quantity of water; the liquid filtered from sulphate of lead; and sulphite of soda added. Iodide of potassium will now precipitate the thallium.

#### THALLIUM AND CADMIUM.

These two metals frequently occur together. The thallium may be detected by adding bichromate of potash, and then excess of ammonia to the acid solution of these metals: the insoluble chro-

mate of thallium will then be precipitated. Commercial sulphide of cadmium, as sold for artists' use, varies considerably in tint, some specimens being of a much deeper orange than others. I have frequently found thallium in the dark-coloured varieties, and it is therefore probable that the variations of colour in sulphide of cadmium are due to traces of thallium. As an instance of a highly thalliferous sulphide of cadmium, I may especially mention a beautiful specimen from Nouvelle Montagne, which formed a prominent object in the Belgian Department of the Exhibition of 1862.

#### THALLIUM AND TIN.

An alloy of thallium and tin is readily obtained by fusion under cyanide of potassium or coal gas. With 5 per cent. of thallium, the alloy is perfectly malleable. When these two metals occur together in a liquid, they may be separated by adding an excess of sulphide of ammonium to the alkaline solution. Sulphide of thallium will be precipitated, whilst the tin will remain in solution.

#### THALLIUM AND LEAD.

These two metals readily melt together, forming a malleable alloy. In analytical operations, they may be separated like thallium and bismuth; or the lead may be precipitated as sulphate, whilst the sulphate of thallium will remain in solution. Sulphuretted hydrogen in an acid solution will also precipitate the lead, and leave the thallium dissolved.

#### THALLIUM AND IRON.

Certain kinds of iron pyrites constitute the richest source of thallium hitherto met with. At the commencement of this paper, I have fully described the methods of separating thallium from thalliferous pyrites on the large scale. The new metal may be readily detected in thalliferous pyrites in the following manner:—Dissolve the finely powdered mineral in nitro-hydrochloric acid; evaporate with excess of sulphuric acid until the nitric acid is evolved; dissolve in water; and add sulphite of soda to reduce the iron and thallium to the state of proto-salts. On adding a little iodide of potassium, and allowing the liquid to stand for some time, a bright yellow precipitate of iodide of thallium will separate. This test is sufficiently delicate to show thallium in a

pyrites which does not contain more than 1 part in 10,000. I have frequently found thallium when working upon no more than ten grains of pyrites.

#### THALLIUM AND COPPER.

It is difficult to make an artificial alloy of thallium and copper containing much of the former metal. When thallium is projected into a crucible containing melted copper, it boils, and in great part volatilises, some however uniting with the copper. By repeated additions of thallium, I have succeeded in forming a hard, brittle, white alloy. With a still smaller quantity of thallium the mixture is gold-coloured; and with 95 per cent. of copper, it forms a hard button, flattening somewhat under the hammer, but soon cracking at the edges. In small quantities, thallium appears to diminish the malleability and ductility of copper. Copper prepared in Spain by the cementation process already described at the commencement of this paper, frequently contains considerable quantities of thallium. A specimen kindly lent me by Dr. Matthiessen, which had a conducting power for electricity of about 15, that of pure copper being 100, was found to contain a large quantity of thallium: it is probable that the pre-eminently bad quality of this copper is to be thus accounted for. When the two metals occur together analytically, they may be easily separated by adding to the acid solution sulphurous acid in excess, and then iodide of potassium; a dirty white precipitate will fall, consisting of subiodide of copper and iodide of thallium. On adding ammonia to the washed precipitate, the iodide of copper rapidly dissolves, with absorption of atmospheric oxygen, to a deep blue liquid, whilst the iodide of thallium is left behind as an insoluble yellow powder. Sulphuretted hydrogen in an acid solution also separates the copper, but as metallic sulphides are very liable to carry down sulphide of thallium, I prefer using other means of separation, if sulphuretted hydrogen can be avoided.

#### THALLIUM AND MERCURY.

The two metals unite readily, forming a solid crystalline amalgam. I have found no process better for separating them analytically than by the use of sulphuretted hydrogen. From per-salts of mercury the gradual addition of iodide of potassium effects a ready separation. If much mercury is present, the precipitate

is almost pure scarlet, but on further addition of iodide of potassium, drop by drop, the iodide of mercury dissolves and leaves the insoluble yellow iodide of thallium.

#### THALLIUM AND GOLD.

*Double Chloride of Thallium and Gold.*—When a hot aqueous solution of chloride of thallium is mixed with a slight excess of chloride of gold, brilliant gold-coloured crystals are deposited, which increase as the solution cools; these consist of a double chloride of gold and thallium. They are difficultly soluble in water, and at a red heat leave an alloy of gold and thallium.

#### THALLIUM AND PLATINUM.

*A. Alloy of Thallium and Platinum.*—These two metals combine together with incandescence. If a piece of metallic thallium is placed on a platinum wire-loop, and held in the flame of a spirit-lamp, they rapidly melt together, becoming nearly white hot, and evolving abundant fumes of thallium; the resulting alloy is highly crystalline, very hard, and almost as brittle as glass. The most convenient way of obtaining the green light of thallium is to alloy a platinum wire-loop in the above manner. When this is introduced into a spirit lamp, or heated before the blowpipe, a green tint of extraordinary splendour is communicated to the flame.

*B. Double chloride of Thallium and Platinum.*—This salt is precipitated in the form of a very pale yellow crystalline powder when bichloride of platinum is added to an aqueous solution of a salt of the protoxide of thallium. When heated to redness, it leaves an alloy of thallium and platinum, the latter metal continually volatilising, until, after being kept for some time at nearly a white heat, the platinum is almost free from thallium. This is the most insoluble salt of thallium I have yet met with, one part requiring no less than 15585 parts of water at 60° F., or 1948 parts of boiling water to dissolve it. The great insolubility of this compound having been considered a reason for classing thallium with potassium, it may be of interest to compare it with the corresponding potassium, ammonium, rubidium, and caesium salts. It will be seen that its degree of solubility gives it very little relationship to these metals.

One part of Chloro- platinate of—	Water at 60° F.	Boiling water.
Potassium dissolves in	108 parts	19 parts.
Ammonium „ „	150 „	80 „
Rubidium „ „	740 „	157 „
Cæsium „ „	1308 „	261 „
Thallium „ „	15585 „	1948 „

## ORGANIC COMPOUNDS OF THALLIUM.

Thallium appears to have some tendency to form organic compounds; only a very limited number have, however, been as yet prepared. Its compounds with organic acids are, for the most part, colourless, except the ferrocyanide and the picrate; they are soluble in water, and generally crystallise with remarkable facility.

*Formate of Thallium* is prepared by dissolving carbonate of thallium in formic acid; it is very soluble in water, and melts without decomposition below 212° F.; its composition is  $C_2HTlO_4$  (Kuhlmann).

*Cyanide of Thallium* is obtained by mixing a concentrated solution of cyanide of potassium with a saturated solution of carbonate of thallium, or by neutralising oxide of thallium with hydrocyanic acid (Kuhlmann). It is more easily prepared by mixing together strong solutions of cyanide of potassium and nitrate of thallium. It separates in brilliant crystalline plates, not very soluble in water. When heated, the salt decrepitates and fuses easily. When intensely heated on platinum foil, it volatilises without reduction or alloying with the platinum.

*Ferrocyanide of Thallium*.—This salt is precipitated by mixing ferrocyanide of potassium with nitrate of thallium. It forms yellow crystals, slightly soluble in water.

*Cyanate of Thallium* is obtained by mixing alcoholic solutions of cyanate of potash and acetate of thallium. It is precipitated in small brilliant plates, very soluble in water and very slightly soluble in alcohol (Kuhlmann).

*Sulphocyanide of Thallium*.—This is a very beautiful salt; it is precipitated by adding sulphocyanide of potassium to a soluble thallium salt. (The per-salts are reduced by it to proto-salts). It falls as a dense crystalline and brilliantly white powder which, when crystallised from hot water, forms brilliant prisms sometimes two inches long.

*Ethylate of Thallium.*—Absolute alcohol is decomposed by thallium, with evolution of hydrogen, when the two are heated together in a sealed tube in a water-bath (Church). When pure thallium in a finely divided state (and partially oxidised on the surface) has absolute alcohol poured over it, the spirit becomes slightly opalescent. In the course of a few hours, this opalescence disappears, and needle-shaped crystals, together with a few drops of a colourless heavy liquid, form in the alcohol. After standing with partial exposure to the air for some days, the thallium dissolves in quantity, and a considerable amount of the oily liquid accumulates. The supernatant alcoholic liquid is unaffected by dilution with water, and acts in every respect like a strong solution of protoxide of thallium. The oily liquid is a compound of protoxide of thallium and alcohol; it is decomposed upon the addition of water, solidifying to a yellow crystalline mass of protoxide of thallium, which dissolves on further addition of water and heating. It makes a greasy stain upon paper, and is almost insoluble in alcohol. Lamy prepares it by dissolving protoxide of thallium in alcohol and evaporating on a water-bath; he describes it as a heavy oily liquid, not boiling at  $212^{\circ}$  F. Its specific gravity is 3.5, and its refracting power is almost as great as that of bisulphide of carbon.

*Acetate of Thallium.*—This salt is prepared by dissolving carbonate of thallium in a slight excess of glacial acetic acid, and evaporating to dryness over a water-bath. The residue is then gently heated on a sand-bath, till it fuses, and no more odour of acetic acid is perceptible. The fused mass is dissolved in water, filtered from a small quantity of a dark precipitate which is usually formed, and then gently evaporated over the water-bath. The salt separates in long silky prisms or plates of a pearly lustre. When heated in an air-bath, they undergo no change until the temperature rises to  $240^{\circ}$  F., when they fuse to a colourless oily liquid, no evolution of gas or other decomposition taking place. Upon cooling, the liquid solidifies to a mass of white radiating crystals, having a beautiful satiny lustre. They bear an hour's exposure to a temperature of  $340^{\circ}$  F. without decomposition, but at a slightly higher temperature, an empyreumatic odour is observed, and the mass on solidifying becomes slightly brown.

The crystals are anhydrous when dried over sulphuric acid at the ordinary temperature; they have no odour of acetic acid; they deliquesce in a cold damp atmosphere, but are permanent in

ordinary dry air; they are very soluble in water and alcohol, and crystallise from the latter with great facility. Their aqueous solution will bear ebullition without loss of acetic acid. Sulphuretted hydrogen instantly precipitates the metal as sulphide. Upon analysis the crystals yielded numbers closely agreeing with the formula  $C_4H_3TlO_4$ .

*Oxalate of Thallium.*—This salt is readily prepared by boiling together equivalent quantities of carbonate of thallium and oxalic acid, in just sufficient water to dissolve the product when hot. Upon cooling, oxalate of thallium crystallises out in the form of small prisms, brilliantly white and lustrous. It may also be prepared by mixing together saturated aqueous solutions of nitrate of thallium and oxalate of ammonia. The salt bears a temperature of  $400^\circ$  F. without change. At  $480^\circ$  F. it becomes slightly discoloured, but scarcely loses any appreciable weight. Upon ignition the crystals decompose, leaving a residue of oxide and metal. They are not very soluble in water and are insoluble in alcohol. One part of the salt requires 69·3 parts of water at  $60^\circ$  F. and 11 parts of boiling water to dissolve it. Hydrochloric acid poured over the dry crystals converts them into a porous spongy mass of chloride. Analyses show that the formula of the salt is  $C_2TiO_4$ . Kuhlmann has analysed it with the same result.

*Binoxalate of Thallium.*—On boiling together two equivalents of oxalic acid and one of carbonate of thallium, the binoxalate is deposited, on cooling, in the form of large plates, having a pearly lustre, and containing water of crystallisation, which is driven off at a temperature of  $270^\circ$  F.; the formula of the dried salt is  $C_4HTiO_8$ . The hydrated crystals appear to be slightly efflorescent, and contain two atoms of water of crystallisation. One part dissolves in 18·7 parts of water at  $60^\circ$  F., and in less than its own bulk of boiling water, forming a syrupy solution; it is strongly acid to test paper.

*Malate of Thallium* crystallises with difficulty; it is deliquescent and melts below  $212^\circ$  F. (Kuhlmann).

*Tartrate of Thallium.*—The neutral tartrate is deliquescent and crystallises with difficulty. It is slightly soluble in water and alcohol. The crystals are anhydrous; heated to  $338^\circ$  F., they carbonise; at a higher temperature, they leave a mixture of a yellow oxide and a little reduced metal. The formula is  $C_8H_4Ti_2O_{12}$  (Kuhlmann).

*Bitartrate of Thallium* is precipitated in a crystalline form when



tartaric acid is added to a solution of neutral tartrate of thallium. Its composition is  $C_8H_5TlO_{12}$  (Kuhlmann).

*Tartrate of Thallium and Antimony.*—When oxide of antimony is treated with a solution of bitartrate of thallium, a double salt is produced, moderately soluble in water, crystallising in needles and efflorescing when dried (Kuhlmann).

*Paratartrate of Thallium* is very soluble in water, and yields groups of crystals, which appear to belong to the prismatic system. Its composition is  $C_8H_4Tl_2O_{12}$  (Kuhlmann).

*Urate of Thallium* is almost completely insoluble, and is obtained by double decomposition between urate of potash and carbonate of thallium (Kuhlmann).

*Valerate of Thallium* has the greatest analogy to the acetate, and, like it, is very soluble in water and in alcohol. Its formula is  $C_{10}H_9TlO_4$  (Kuhlmann).

*Picrate of Thallium* crystallises in silky plates resembling crystals of picrate of potash (Kuhlmann).

*Citrate of Thallium* is very deliquescent, and crystallises with difficulty. It is slightly soluble in alcohol; its composition is  $C_{12}H_5Tl_3O_{14}$  (Kuhlmann).

*Benzoate of Thallium* crystallises in pearly plates, and is not volatile (Kuhlmann).

*Thallium-benzamide.* This compound has been examined jointly by Professor Church and the author. It is prepared by adding pure benzamide to a hot aqueous solution of pure protoxide of thallium. The benzamide dissolves freely, and the excess crystallises out on cooling. Upon adding a large excess of absolute alcohol to the filtrate, thallium-benzamide is immediately precipitated. This body crystallises in fine needles, soluble in both hot and cold water, forming a highly alkaline solution. Its insolubility in alcohol affords a ready means of purification both from benzamide and from oxide of thallium. When heated, it melts without decomposition, at a higher temperature becoming dark coloured, and evolving white inflammable vapours, which burn with a smoky flame tinged with green. At a red heat, all organic matter is dissipated, a fusible residue of oxide of thallium being left behind. Its composition is  $C_{14}H_5O_2$   $\left. \begin{matrix} Tl \\ H \end{matrix} \right\} N$ .

It has many properties in common with its analogues, argento- and mercurio-benzamide, although, as might have been anticipated



from the peculiarities of its metallic ingredient, it differs from them in several particulars. Hydrochloric acid, added to the compound, occasions an immediate precipitate of chloride of thallium, benzamide being separated at the same time.

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