

2. That pressure alone is not the cause of the deformity.

3. That besides the softening effect of continuous moisture acting for ages upon the cartilaginous or animal matter of the bones, there is proof of the presence of free carbonic and nitric acids very generally in soils, and more particularly in black mould, such as that of the Orchard at Wroxeter.

4. Nitric acid may also be discovered in small quantity. But carbonic acid is almost always present in soil where air and moisture come in contact with organic matters in a state of decomposition. He thinks that this is the principal cause of the solution of bone in the earth, rendering it softer, and more ready to bend or break.

5. That the distortion must occur at a comparatively early period after interment, because when all, or nearly all, the animal matter of the bones is destroyed, they cannot bend.

Lastly. That some of the apparently *bent* bones are really *broken*; Professor Wyville Thomson, of Belfast, having first pointed out to the author minute cracks or fissures in some of the distorted crania.

VIII. "Preliminary Researches on Thallium." By WILLIAM CROOKES, Esq., F.C.S. Communicated by Professor STOKES, Sec. R.S. Received June 19, 1862.

Having so recently been honoured by the Council of the Royal Society with a grant from the Donation Fund for the purpose of defraying some of the expenses of my researches on this new element, I should not have ventured to offer to the Society so incomplete a notice as the present one, had I not within the last week heard that a continental chemist, Professor Lamy, of Lille, has recently been fortunate enough to meet with a residue containing thallium in considerable quantities, and has isolated the element and prepared several of its compounds: it therefore appears advisable at once to place on record a description of several compounds of this body obtained since the date of my first announcement of its discovery in March 1861, but which I had purposely avoided publishing in order that it might form part of a more complete memoir on the subject which I had hoped at some future day to have the honour of sub-

mitting to this Society. I trust that, under these circumstances, I may be pardoned for bringing before the Royal Society an incomplete account of this new element.

The occurrence of a brilliant green line in some selenium residues, whilst examining them for tellurium, led me first to suspect the presence of a new element. This had been derived from a considerable quantity of the seleniferous deposit from the sulphuric acid manufactory at Tilkerode in the Hartz Mountains, which had been kindly placed at my disposal by Professor Hofmann; and the residue was that left behind on distilling the selenium which had been prepared from the deposit by appropriate chemical treatment. The processes through which it had passed limited the elements which could by any possibility be present to some half dozen; and as I was pretty confident that none of these presented in the spectro-scope the phenomenon of a single bright-green line, it became of interest to investigate the subject further. In March 1861* I was enabled to announce definitely that the green-line substance was decidedly a new element, and that from some of its reactions it was probably a high member of the sulphur, selenium, and tellurium group, although I hesitated to assert this positively. The paper alluded to contained a sufficient number of the reactions of this body to enable me to prove chemically, as well as optically, that I was dealing with a new element possessing well-defined characters. Pursuing the investigation, I was enabled in the following May† to give a further account of this body, and to propose for it the name of *Thallium* (symbol *Tl*), from the Greek θαλλός, or Latin *thallus*, a budding twig,—a word which is frequently employed to express the beautiful green tint of young vegetation, and which I chose on account of the green line which it communicated to the spectrum recalling with peculiar vividness the fresh colour of early spring. In the same note I gave the localities and description of several minerals in which I had found the element, and also a method of extracting it from them in a pure state. Considering that I had sufficiently announced the discovery in these papers, which were republished in nearly every chemical journal in Europe, I turned my

* Philosophical Magazine, S. 4. vol. xxi. p. 301; and Chemical News, vol. iii. p. 194, March 30, 1861.

† Chemical News, vol. iii. p. 303, May 18, 1861.

attention towards procuring a source of thallium which would enable me to prepare this body on the large scale ; my experiments having hitherto been confined to mineralogical specimens which I had difficulty in tracing to their source, and the whole amount of thallium which I had as yet obtained not exceeding three grains in weight.

After some delay, Mr. Thornthwaite was good enough to supply me with a considerable quantity of crude sulphur distilled from Spanish copper pyrites. In this I found thallium present to the extent of one or two grains to the pound, and up to within the last few months it has been from the element prepared from this source that I have been working. I have recently, however, succeeded in finding an ore containing thallium, which is worked in this country, and from which I hope to be able to prepare the metal in larger quantities.

I have found the following the most advantageous method for extracting the new element from sulphur or pyrites :—

Powder the ore very finely, and dissolve it as completely as possible in strong hydrochloric acid, with gradual addition of nitric acid until all solvent action ceases ; then dilute with water, and filter. Evaporate down to drive off the excess of nitric acid, add a little sulphuric acid if necessary, and take care that the solution does not get dry, or even pasty. Then dilute with water, and heat gently, to be certain of getting all the soluble portion dissolved. Filter : if lead be present, the greater portion will be left behind in this operation in the form of insoluble sulphate. Dilute the filtrate considerably, and add a solution of carbonate of soda until the reaction is distinctly alkaline ; then add an excess of solution of cyanide of potassium (free from sulphide of potassium). Heat gently for some time, and then filter. 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 now being passed through the liquid, precipitates all the thallium, whilst the copper, antimony, tin, and arsenic remain dissolved. If cadmium and mercury are present, they will accompany the thallium. The former can readily be dissolved out by warm dilute sulphuric acid, which has scarcely any solvent action on the sulphide of thallium, whilst this in its turn can be separated from the sulphide of mercury by being boiled in moderately dilute nitric acid, in which the sulphide of mercury is insoluble.

These two metals are, however, seldom present with thallium in the ores which I have examined. The nitric-acid solution is now to be evaporated to dryness, the residue dissolved in hot dilute sulphuric acid, and a piece of pure metallic zinc placed in the liquid; the thallium will be at once precipitated in the form of a deep-brown powder, which soon changes to a heavy black, granular precipitate. The metal can be obtained in the coherent form by fusion in hydrogen.

This method of analysis is given on the supposition that all the above metals are present. It may generally be much abridged, as the ore is seldom of so complicated a character. If there is a difficulty in procuring perfectly pure zinc for the reduction of the sulphate to the metallic state, this can be effected by passing a weak voltaic current through the liquid, using platinum poles; the metal will then be precipitated in the reguline, or spongy state, according to the strength of the current. I have not been very successful in reducing the oxide by hydrogen. The current of gas carries the volatile oxide away from the heated part of the tube before complete reduction takes place. It is, however, probable, from an observation made towards the conclusion of this experiment, that, with a longer tube in proportion to the quantity of material, kept at a good heat throughout its length, this plan might give good results, the metal being considerably less volatile than the oxide.

In many cases, when minute traces only of thallium accompany large quantities of other metals, it may be advisable to repeat the whole or some of the above operations, in order to purify this element from foreign metals which may have escaped complete removal.

I now pass on to a description of thallium and its chemical reactions.

Thallium in the pure state is a heavy metal, bearing a remarkable resemblance to lead in its physical properties. Its specific gravity is, however, higher—about 12. The freshly scraped surface has a brilliant metallic lustre not quite so blue in colour as lead, and it tarnishes more rapidly than this latter metal. It is very soft, being readily cut with a knife and indented with the nail; it may also be hammered out and drawn into wire, but has not much tenacity in this form. It easily marks paper. The fusing-point is below redness, and with care several pieces may be melted together and cast into one lump.

There is, however, generally a loss in this operation, owing to its rapid oxidation. The metal itself does not appear to be sensibly volatile below a red heat. I have made no special attempts at present to determine the atomic weight, although from two estimations of the amount of sulphur in the sulphide it appears to be very heavy. The figures obtained did not, however, agree well enough to enable me to speak more definitely on this point, than that I believe it to be above 100. I may mention that I obtained this element in the pure metallic state and exhibited it to several friends as early as January last *, and should then have published an account of it, had it not been for the reasons already mentioned. Thallium is soluble in nitric, hydrochloric, and sulphuric acids, the former attacking it with greatest energy, with evolution of red vapours.

Oxides of Thallium.—Thallium forms two, and probably three oxides: one possessing basic properties, which I shall call the oxide; another containing more oxygen, possessing acid properties, which may therefore be called thallic acid; and most likely a third, or suboxide, which forms the first portions of the precipitate formed by zinc in solutions of this metal; the first action being a darkening of the solution, and the production of a deep-brown powder, which by longer contact with zinc turns to a dense black precipitate.

Upon carefully evaporating the nitric-acid solution upon a water-bath, but not carrying it to dryness, a mass of deliquescent crystals is obtained on cooling, which are decomposed upon addition of water with separation of a white or pale-yellow precipitate, which appears to be a subnitrate, and an acid solution containing nitrate of thallium. If the liquid is evaporated quite to dryness and kept at a temperature of 100° C. for a little time, the nitric acid goes off, and leaves a residue of thallic acid.

Thallic Acid.—This acid is soluble in water, and may be obtained in the crystalline form from its aqueous solution. It then forms crystals, which are permanent in the air, and have an acid reaction to test-paper. The thallates of the alkalis are also soluble in water, and may be prepared by dissolving the acid in the alkali, or by fusing thallium or its oxide with a mixture of alkaline carbonate and nitrate. The method I originally published for extracting thallium was based

* Vide Chemical News, vol. v. pp. 349, 350.

upon the formation in this manner of an alkaline thallate soluble in water. This acid is also produced in solution when permanganate of potash is added to a soluble salt of oxide of thallium.

Chloride of Thallium.—If a current of dry chlorine is passed over precipitated thallium at a moderate heat, they combine with formation of a volatile chloride, which condenses in the cool part of the tube in the form of a pale-yellow crystalline powder, fusing together in parts to a crystalline lump. Water only partially dissolves this, with production of a white insoluble residue. Dilute hydrochloric acid added to the turbid solution immediately renders it clear; upon evaporating this solution over a water-bath, white crystals of the chloride are deposited. When the nitric-acid solution of thallium or its sulphide is evaporated with an excess of hydrochloric acid, and then more hydrochloric acid added and the evaporation repeated to a syrup, a residue is obtained which is apparently decomposed by water with production of a white precipitate: this is chloride of thallium; it is insoluble or nearly so in water, but readily soluble in dilute hydrochloric or nitric acid.

Sulphide of Thallium.—When sulphuretted hydrogen is passed through the acid solution of chloride of thallium, a partial precipitation of a reddish-brown powder takes place; this appears to be a combination of the chloride and sulphide, and the metal is never entirely removed from solution by this means. The best method of obtaining the sulphide is to precipitate it with sulphide of ammonium in an alkaline solution: unless a large quantity of thallium is present, no immediate effect is produced beyond the darkening of the liquid; it assumes a brown tint, which becomes rapidly more and more intense, especially upon gently heating it, until the sulphide of thallium separates in the form of a deep-brown heavy precipitate which shows a great tendency to collect together in clots at the bottom of the vessel: this formation of the sulphide is very characteristic of the metal. Sulphide of thallium is insoluble in an excess of sulphide of ammonium, ammonia, or cyanide of potassium. Its complete precipitation as sulphide from solutions containing an excess of cyanide of potassium affords a ready means of separating thallium from several metals with which it is frequently associated. It is difficultly soluble in hydrochloric or sulphuric acids, but readily

so in nitric acid. When dry, it is a deep-brown, almost black powder, fusing and volatilizing when heated : when pure, it is neither so fusible nor so volatile as sulphur ; but when it occurs with an excess of this latter element, it is very difficult to separate from it by sublimation.

Carbonate of Thallium is precipitated upon adding an alkaline carbonate to the acid chloride solution ; it is moderately soluble in an excess of carbonate of ammonia, and readily so in cyanide of potassium. This is a very definite reaction, and enables thallium to be separated with accuracy from lead and bismuth.

Sulphate of Thallium.—When the hydrochloric or nitric solution is evaporated down with sulphuric acid, the more volatile acid is driven off and the sulphate is left behind. It is crystalline and soluble in water.

Iodide of Thallium is precipitated as a yellowish-red powder upon cautious addition of iodide of potassium to a solution of thallium. It is readily soluble in excess of iodide of potassium, forming a colourless solution.

Phosphate of Thallium forms a white flocculent precipitate soluble in mineral acids, but sparingly soluble in acetic acid.

Ferrocyanide of Thallium is white and insoluble in water.

Cyanide of Thallium is precipitated as a white or light-brown powder upon the cautious addition of cyanide of potassium to a solution of thallium. It is readily soluble in an excess of the precipitant.

Chromate of Thallium is a pale-yellow precipitate soluble in acids and reprecipitated upon neutralization with ammonia.

No precipitates are produced when a solution of thallium is mixed with *protochloride of tin*, *oxalic acid*, *carbazonic acid*, *sulphurous acid*, or *protosulphate of iron*.

Most of these reactions have been independently verified by my friends E. O. Brown, Esq., and J. Spiller, Esq., of the Chemical Department, Woolwich Arsenal ; and I am glad to be enabled to take this opportunity of expressing my obligations to them for their valuable aid. The reactions are sufficient to prove chemically that the body under examination is a new element. Its behaviour in the spectrum apparatus is perhaps the most conclusive test upon this

point. When a minute portion of the metal (the sulphide, chloride, or, in fact, any compound of thallium) is introduced into the flame of the spectroscope, it immediately produces a single green line, perfectly sharp and well defined upon a black ground, and of extraordinary purity and intensity, almost equal to the sodium-line in brilliancy. It is not, however, very lasting. Owing to its great volatility, a portion introduced at once into the flame merely shows the line as a brilliant flash, remaining only a fraction of a second; but if it be introduced into the flame gradually, the line continues present for a much longer time. If, also, a piece of metallic thallium be introduced into the flame on a platinum wire loop, they fuse together, and the alloy gives the green line rather more permanently, although of course fainter.

Working on a small scale, it is not easy to obtain these compounds free from soda; but when that is effected, and a tolerable quantity of substance is held on a loop of platinum wire in a flame, the green colour is most brilliant, and produces very extraordinary effects upon the appearance of surrounding objects. If thallium could be obtained in quantity, this ready means of producing an intense and homogeneous green light could not fail to be applicable to some useful purpose.

The green line of the thallium spectrum appears to be unaccompanied by any line or band in other parts of the spectrum. A flame of sufficient temperature to bring the orange line of lithium into view produces no addition to the one thallium-line; and an application of telescopic power strong enough to separate the two sodium-lines a considerable distance apart still shows the thallium-line single. I consider therefore that I am justified in stating that thallium produces *the simplest spectrum of any known element*. Theoretical inquiries into the cause of the spectrum lines, and their relation to other constants of an element, may be facilitated now we know a metal which gives rise to luminous vibrations of only one degree of refrangibility. The remarkable simplicity of the thallium spectrum offers a strong contrast to the complicated spectra given by mercury, bismuth, and lead—the metals to which it has the most chemical resemblance.

The position of the green line does not coincide with any definite line in the solar spectrum. According to Kirchhoff's theory, we must

therefore assume that thallium is not present to any great extent in the sun. Under the highest telescopic power of my apparatus, the line appears to be absolutely identical in refrangibility with a sharp well-defined line in the barium spectrum, to which Professors Bunsen and Kirchhoff have given the name $Ba\delta$. Want of material has hitherto prevented me from taking accurate measurements of the distance between the thallium-line and the principal lines of the solar spectrum.

This green line is an exquisitely delicate test for the presence of thallium, and shows it to be a somewhat widely distributed element. Many specimens of crude sulphur contain it (especially when rather dark-looking). In most cases it is only necessary to set fire to as large a piece of sulphur (less than a pea) as the platinum loop will hold, and when it has nearly burned away to blow it out, and then introduce it at leisure into the flame of the spectroscope, for the thallium to show its presence by a bright-green line which will flash for an instant into the field of view. Although the greater part of the thallium is left behind after burning off the excess of sulphur in this manner, some of it volatilizes, and consequently, if the specimen gives no indications of thallium by this treatment, it will be advisable to dissolve out as much of the sulphur as possible with bisulphide of carbon, and then to test the residue in the flame.

Thallium is a constituent of very many mineral ores. Upon examining a large collection of cupriferous pyrites from different parts of the world, I found it present in more than one-eighth. It is not confined to any particular locality; neither does it seem to bear any relation to the presence or absence of arsenic in the mineral. I have, however, very rarely met with it in pyrites in which copper was absent. In most cases it is only necessary to powder a small fragment of the mineral and ignite a little of it in the flame on a moistened platinum wire, for the green line to be distinctly visible.

If a thalliferous pyrites is finely powdered and then heated to redness in a glass tube, as much as possible out of contact with air, the sulphide of thallium, together with some free sulphur, sublimes from it and may be condensed by appropriate arrangement. This sublimate gives the thallium-line with great brilliancy.

Owing to the frequent occurrence of thallium in copper ores, it is very probable that this element may sometimes be present in commercial copper, and may give rise to some of the well-known, but unexplained, differences of its quality. I am at present engaged in investigating this subject, and have already found some indications of thallium in commercial products.

I have no hesitation in saying that in some of our large copper, sulphur, and sulphuric-acid works, thallium is at the present time being thrown away by the hundredweight: a very slight modification of the present arrangements of the furnaces and condensing flues, or even an examination of some of the residues, would enable nearly the whole of this to be saved. Bearing this in view, I am now in communication with several large consumers of thalliferous minerals. My applications have without exception been met with the utmost courtesy and most obliging offers of assistance, and there is therefore every probability that I shall soon have an opportunity of preparing this new element in considerable quantities, and thus be enabled to pursue the investigation with more comfort and accuracy than hitherto, when my stock of material has had to be counted by the grain.

- IX. "On the Photographic Transparency of various Bodies, and on the Photographic Effects of Metallic and other Spectra obtained by means of the Electric Spark." By Prof. W. ALLEN MILLER, M.D., LL.D., V.P. and Treas. R.S. Received June 19, 1862.

(Abstract.)

In this paper the author pursues an inquiry the commencement of which was communicated to the Chemical Section of the British Association last year. Owing to the employment of a prism of bisulphide of carbon, he was then led to believe that the photographic effects of the electric spectra produced by the different metals were in a great degree similar, if not identical. Subsequent investigations have, however, shown him that the absorbent effects of the bisulphide upon the chemical rays are so great, that the conclusions then drawn from observations made by this refracting medium require