



Philosophical Magazine Series 3

ISSN: 1941-5966 (Print) 1941-5974 (Online) Journal homepage: http://www.tandfonline.com/loi/tphm14

On a new metal, pelopium, contained in the **Bavarian tantalite**

Prof. H. Rose

To cite this article: Prof. H. Rose (1846) On a new metal, pelopium, contained in the Bavarian tantalite, Philosophical Magazine Series 3, 29:195, 409-416, DOI: 10.1080/14786444608645529

To link to this article: http://dx.doi.org/10.1080/14786444608645529



Published online: 30 Apr 2009.



Submit your article to this journal





View related articles 🗹

Full Terms & Conditions of access and use can be found at http://www.tandfonline.com/action/journalInformation?journalCode=tphm14 The author is of opinion that the evidence on which the modern theory of the composition of water is founded, is fallacious; and believing water to be a simple body, he conceives that it forms hydrogen by combining with the electric fluid, which he imagines to be identical with the phlogiston of former chemists. He cites the opinions of Priestley, Cavendish and Watt, as corroborating his views, and interprets their experiments in conformity with the hypothesis he has adopted.

"Suggestion intended to confirm Franklin's Theory of Electrostatics, by explaining the phenomena of Repulsion between bodies negatively electric." By James A. Smith, Esq. Communicated by S. Hunter Christie, Esq., Sec. R.S., &c.

The author conceives that in negatively electrified bodies, or bodies having less than their natural quantity of electricity, the redundant matter must have a tendency to escape, and thus the equilibrium of its cohesion is destroyed; and that two bodies in such a condition must mutually repel each other.

"On Sir Isaac Newton's Method of Finding the Limits of the Roots of Equations." By Herbert Panmure Ribton, Esq. Communicated by John George Children, Esq., F.R.S.

The author states that he has reason to believe that by generalizing from successive inductions of equations, a formula more universal than Newton's Binomial could be found.

LX. Intelligence and Miscellaneous Articles.

ON A NEW METAL, PELOPIUM, CONTAINED IN THE BAVARIAN TANTALITE. BY PROF. H, ROSE.

I N a former paper, on the composition of the so-called tantalic acid which occurs in the columbite of Bodenmais in Bavaria, I showed that it consisted of two acids, one of which differs so decidedly from all known metallic oxides, that I did not hesitate to regard it as the oxide of a new metal, which I named niobium*. I did not then enter into a description of the second acid, which occurs in company with the niobic acid, but merely observed that it possessed great similarity to the tantalic acid procured from the Finland tantalites.

The separation of the two acids according to the method I formerly described was exceedingly troublesome and tedious. After I had suspected a peculiar substance in the so-called tantalic acid from columbite, and had vainly attempted in various ways to isolate it, I succeeded in effecting this only approximatively on converting the acid into chloride, by mixing it with charcoal and passing a current of chlorine over the heated mixture. I obtained a yellow, readily fusible and very volatile chloride, and a white, infusible, less volatile chloride. Both were converted by water into metallic acids, which were not dissolved by the hydrochloric acid formed, but separated on boiling, and could easily be freed by washing with water from

* The paper here referred to will be found at p. 35 of the third volume of the Chemical Gazette.

410

every trace of acid; but when the acid from the white infusible chloride, after I had separated it as well as possible from the yellow one, was again mixed with charcoal and treated with chlorine, I constantly obtained yellow and white chloride; less, it is true, of the first than when the mixture of the two acids as they occur in the mineral was employed; but even when the operation was very frequently repeated with the acid from the white chloride, it was not possible to obtain by this method a pure white chloride free from vellow. I observed however that the white chloride was only partially sublimed. When it was separated as much as possible from the yellow chloride, and by sublimation also from a white non-volatile residue, it at last afforded an acid, which on treatment with charcoal and chlorine yielded a tolerably pure, white, wholly volatile chloride, the chloride of niobium. The white fixed residue vielded with charcoal and chlorine a large quantity of yellow chloride; and after removing this by sublimation, again left a white nonvolatile residue, which, on being again subjected to a similar treatment, afforded the same products.

On comparing this behaviour of the yellow chloride with that observed on treating a mixture of pure tantalic acid and charcoal with chlorine, I obtained a perfectly similar yellow chloride and a white non-volatile residue; but the quantity was far smaller, and its production could be entirely avoided if, in the preparation of the chloride of tantalium, every trace of humidity and atmospheric air had been carefully excluded. Moreover, the sublimed yellow chloride from the Bavarian mineral very much resembled the chloride of tantalium. This similarity likewise extended to the acids prepared from the two chlorides; they behaved so much alike, that it was only after long-continued investigation properties were discovered by which they might be separated.

Both in the preparation of chloride of tantalium with the tantalic acid from the Finland tantalite, but especially in that of the yellow chloride from the Bavarian mineral, I frequently obtained considerable quantities of a red chloride, which was still more volatile than the yellow one, and proved on examination to be chloride of tungsten. When the chlorides are exposed for some time to the air, the tungsten can be removed by digestion with ammonia as readily soluble tungstate of ammonia.

Sometimes chloride of tin and chloride of titanium were obtained in preparing the chloride; they could be readily distinguished, by their fluid state of aggregation, from the other chlorides.

The formation of the chlorides of tungsten and tin was in so far remarkable, as the acids from which the chlorides were prepared had been kept in a moist condition for a long time in contact with sulphuret of ammonium. I draw especial attention to this circumstance, because, unless perfectly freed from these impurities, the chlorides and the acids prepared from them are obtained with very different properties.

The yellow chloride from the Bavarian mineral differs therefore principally from the chloride of tantalium by its leaving a white non-volatile residue on its production, or rather on its volatilization, at a high temperature. This residue consists principally of the acid which may be obtained from the yellow chloride by decomposition with water.

In the preparation of the yellow chloride from the columbite of Bodenmais, there is formed along with it an oxychloride, which is decomposed by heat into chloride and acid, just like the tungstate of the chloride of tungsten. The formation of the oxychloride can be prevented by placing a long layer of charcoal in the anterior portion of the glass tube, in which the mixture of acid and charcoal is to be treated with chlorine. While the chlorine is passing through the tube, this charcoal is first raised to a strong red heat, and then the mixture.

The acid of the yellow chloride from the Bodenmais mineral, which is contained in it along with the niobic acid, I have named *Pelopic* acid, and the metal *Pelopium*, from Pelops the son of Tantalus and the brother of Niobe; to point out, at the same time, by this name, not only its simultaneous occurrence with the oxide of niobium, but more particularly the very great resemblance of pelopic acid to the tantalic acid from the Finland tantalites. This similarity is indeed more perfect than exists between the combinations of any other two simple metals; it is so great, that it was only after a long-continued and most minute investigation that I could decide upon publishing the results I had obtained. The combinations of niobium are, on the contrary, very different from those of pelopium or tantalium.

I will here describe the most important properties by which the compounds of tantalium differ from the corresponding compounds of pelopium, and at the same time enumerate those of niobium.

In its properties pelopic acid is intermediate between tantalic and niobic acids, just as strontia between baryta and lime. And in the same way as we are able to explain many properties of strontia, by assuming it to be a mixture of the two last-mentioned earths, we are able to determine à priori most of the properties of pelopic acid, by admitting it to be a mixture of a large proportion of tantalic acid with a small quantity of niobic acid; and as was the case with bromine, which, on its discovery, was considered to be a combination of chlorine and iodine, I myself was long of opinion that the pelopic acid was nothing more than tantalic acid still contaminated by a certain quantity of niobic acid, which I had not succeeded in It was only by an uninterrupted investigation of this separating. subject for several years that I became convinced of the distinctness of pelopic acid.

The chlorides of the three metals dissolve in cold concentrated sulphuric acid without any evolution of heat, but with disengagement of hydrochloric acid; but if the solution of the chloride of tantalium and pelopium is boiled, it solidifies to a jelly. Water then does not dissolve any of the tantalic acid, but a large quantity of the pelopic acid. The solution of the chloride of niobium in sulphuric acid is not rendered turbid by boiling; it even remains clear on dilution with water, but if it be now boiled, the whole of the niobic acid is precipitated from the solution.

Intelligence and Miscellaneous Articles.

Chloride of tantalium dissolves in hydrochloric acid in the cold to a turbid liquid, which after some length of time forms an opaline jelly, from which cold and boiling water dissolve only traces of tan-But if chloride of tantalium is treated with boiling hytalic acid. drochloric acid, it does not dissolve entirely, and on cooling it does not form a jelly, but water now dissolves the whole of it to an opaline liquid, which is not rendered more turbid by boiling. Sulphuric acid produces in it, after some time, a voluminous precipitate even in the cold. The chloride of pelopium behaves in a similar manner, except that sulphuric acid does not produce a precipitate in the cold in the solution obtained by boiling and diluted with water, but only Chloride of niobium does not dissolve in cold hydroon boiling. chloric acid; scarcely anything is dissolved on the addition of water; when however chloride of niobium is boiled with hydrochloric acid, it does not dissolve in it, but on diluting with water the whole dissolves, and the niobic acid is not even precipitated from the solu-When however sulphuric acid is added, a turbidtion by boiling. ness results even in the cold, and the whole of the niobic acid is precipitated by boiling. When, on the other hand, but a small quantity of hydrochloric acid is placed in contact with the hydrates of the acids, the result is quite a different one. The same is the case when the chlorides of the three metals are treated with much The niobic acid is then completely separated on boiling from water. the chloride of niobium, and also the pelopic acid from the chloride of pelopium; but tantalic acid does not separate quite so completely from the chloride of tantalium.

Chloride of tantalium, heated with a solution of hydrate of potash, is partly dissolved; but a solution of carbonate of potash does not dissolve any tantalic acid even on boiling. Chloride of pelopium is dissolved in large quantity by solution of caustic potash, and even carbonate of potash dissolves it in tolerable abundance on boiling. Chloride of niobium is dissolved even in the cold by a solution of potash, and also by boiling in a solution of carbonate of potash.

Tantalic acid remains white on being heated to redness; pelopic acid is rendered slightly yellowish; niobic acid, dark yellow. On cooling, both again become as white as before ignition.

All three acids exhibit, when their hydrates are heated very strongly, the phænomenon of incandescence. This however is not the case when the compounds with sulphuric acid are treated with ammonia, and then heated to redness.

Tantalic acid, exposed in a current of hydrogen to a strong red heat, remains white; pelopic and niobic acids become black; but the reduction which these acids undergo is quite inconsiderable, for very doubtful traces of water are perceptible, and the blackened acids quickly become white when heated with access of air, without experiencing any perceptible increase in weight. When tantalic acid is heated to redness in a current of gaseous ammonia in a brisk charcoal fire, it is turned gray, with the formation of but slight traces of water. Pelopic and niobic acids become black, and are reduced, with the production of a considerable quantity of water.

When tantalic acid is heated in a brisk charcoal fire, and sulphu-

retted hydrogen gas passed over it, it becomes slightly gray, but no trace of water is perceptible. Pelopic and niobic acids are converted by the same treatment slowly but entirely into sulphurets, with formation of water and separation of sulphur.

Metallic pelopium can be prepared from the chloride by treatment with ammonia, in the same way as the metals from the chloride of tantalium and chloride of niobium. It has the greatest resemblance to tantalium.

When the ignited acids, which are insoluble in almost all reagents in the moist way, are fused in a silver crucible with hydrate of potash, they dissolve in it. The fused mass is soluble in water. Hydrate of soda behaves in a different manner. When the ignited acids are melted with it, the fused masses obtained are not clear; but an insoluble sediment is formed, which does not dissolve in any excess of the alkali. If the fused mass be treated with a moderate quantity of water, the excess of soda is removed, and a white insoluble mass remains. If, after removing the free soda, a large portion of water be poured over the insoluble mass, it dissolves, and most completely when niobic acid has been employed.

The insolubility of the three acids in excess of soda, while the potash compounds are soluble in excess of potash, essentially characterize them. In this they differ from similar acids, especially When the solutions of the soda salts are mixed from tungstic acid. with concentrated solutions of hydrate of soda, they immediately become turbid; if the mixture was made very slowly and carefully, all three soda salts may be obtained in crystals, which are deposited on the sides of the vessel. But crystals only of the niobate of soda I succeeded in obtaining them can be easily obtained of any size. half an inch and more in size, but in general they are much smaller. They are sparingly soluble in cold, more readily soluble in hot water; the solution may be boiled without becoming turbid; it can be evaporated, and the niobate of soda deprived of its water of crystallization without being decomposed. The salt is only rendered insoluble in water by being heated to redness.

The pelopate, and especially the tantalate of soda, are less stable; when their solutions are boiled, an insoluble white precipitate separates, which is an acid salt of soda.

When the niobate of soda is exposed to a red heat, and a current of dry sulphuretted hydrogen passed over it, a dark black crystalline mass is obtained, from which water removes hydrosulphated sulphuret of sodium, while crystalline sulphuret of niobium remains undissolved.

When pelopate of soda is treated in the same manner, there is also no sulphosalt formed, but only sulphuret of pelopium. The tantalate of soda remains white on treatment with sulphuretted hydrogen, but its soda is converted into sulphuret of hydrogen and sodium.

When niobic acid is fused with an excess of carbonate of soda until the fused mass no longer decreases in weight, the amount of oxygen in the expelled carbonic acid is twice that in the niobic acid employed. The results obtained on fusing pelopic and tantalic acids with carbonate of soda did not agree. By long-continued fusion of tantalic acid with carbonate of soda, so much carbonic acid is expelled that its amount of oxygen was equal to that of the tantalic acid employed, and finally exceeded it. But nevertheless this basic salt does not dissolve undecomposed in water, but leaves a considerable residue of acid tantalate of soda. Something similar takes place with pelopic acid, only the basic pelopate of soda formed dissolves entirely in water.

When the three acids are fused with carbonate of potash, they exhibit similar properties; but the potash salts are as soluble in the excess of carbonate of potash as in hydrate of potash. In this way we obtain compounds which are soluble in water and crystallize; but they contain carbonate of potash, which cannot be separated in any manner.

The combinations of tantalic acid with the alkalies are characterized by their passing on all occasions into insoluble acid salts, especially on boiling and evaporating their solutions. The solutions of the alkaline pelopates exhibit this property in a far less degree, those of the niobates not at all. Insoluble acid niobates of potash or soda can only be produced by not fusing the acid a sufficient time with the carbonates.

Tantalic acid is soon and entirely precipitated from its alkaline solutions by carbonic acid as an acid salt; the same is the case with pelopic acid, but with greater difficulty and far more slowly. It is owing to this that the neutral solution of tantalite of soda becomes turbid even by exposure to the air, while that of the pelopate of soda does not become turbid even after long exposure, which is characteristic of it. Carbonic acid produces a precipitate in the solution of alkaline niobate only after a considerable length of time, which however is again dissolved by much water.

When the solutions of the alkaline tantalates and pelopates are treated with an excess of hydrochloric acid, the eliminated acids dissolve to faintly opaline liquids. Sulphuric acid produces in these solutions precipitates, and separates the acids on boiling; however, only the pelopic acid entirely, and not so the tantalic acid. Hydrochloric acid precipitates the acid from the solutions of the alkaline niobates in the cold, and still more so on boiling; an excess of hydrochloric acid merely dissolves slight traces. This behaviour is in so far interesting, as we have seen that under other circumstances niobic acid may be wholly soluble in hydrochloric acid. Sulphuric acid precipitates niobic acid from its alkaline solutions even in the cold.

From the solutions of the alkaline tantalates the acid is entirely precipitated, without the assistance of heat, by chloride of ammonium, pelopic acid less perfectly, and niobic acid still less.

When the solutions of the alkaline tantalates are rendered acid with hydrochloric or sulphuric acid, a pale yellow precipitate is produced in them by tincture of galls. An orange-yellow precipitate is formed, under similar circumstances, in solutions of the pelopates, and a dark orange-red in those of the niobates. Ferrocyanide of potassium produces in solutions of the tantalates of the alkalies, when they have been rendered slightly acid, a yellow precipitate; in those of the pelopates, a brownish-red; and in those of the niobates, a red one.

When the three acids are fused with bisulphate of potash, they dissolve in it. Niobic acid alone solidifies with it to a crystalline mass. Water removes sulphate of potash from the fused masses, and leaves compounds of sulphuric acid with the metallic acids, from which however the sulphuric acid can be removed by very long treatment with water.

When hydrochloric or sulphuric acid is added to the solution of the niobate of potash or soda, and then a bar of zinc immersed in it, the separated niobic acid soon assumes a very beautiful pure blue colour. It gradually becomes dirtier, and finally brown. The blue colour is produced, in the solutions of the alkaline pelopates, only on the addition of sulphuric acid; but not even then is a blue colour produced in the alkaline tantalates, which however takes place when the solution of the chloride of tantalium in sulphuric acid is treated with water and zinc.

Tantalic acid yields before the blowpipe colourless pearls with the fluxes even in the inner flame; pelopic acid gives with the microcosmic salt in the outer flame a colourless, in the inner one a brown pearl. Niobic acid colours the microcosmic salt in the inner flame of a beautiful blue; the pearl can be easily blown colourless in the outer flame.

These are the most important differences between pelopic acid and tantalic acid on the one hand, and niobic acid on the other. To ascertain accurately the behaviour of these acids and their combinations is one of the most difficult tasks, as all three acids frequently exhibit highly anomalous properties. We have seen, for instance, that the niobic acid is readily dissolved, under certain circumstances, by hydrochloric acid, when separated from its combinations, while under not very dissimilar circumstances it is almost entirely precipitated by it. This is owing to the acid assuming different isomeric modifications.

The three acids resemble in this respect silicic acid, the behaviour of which towards reagents is frequently remarkable, and only excites less surprise from our having been long acquainted with this acid, and its properties having been thoroughly examined.

This tendency of the three acids to assume different isomeric modifications is connected with the great variability which they exhibit with respect to their specific gravity. My experiments on this subject have led me to the most unexpected results; although I have not terminated my investigations, I will nevertheless communicate at present some of the most important.

Some time ago I drew attention to the fact, that in the artificially prepared titanic acid the specific gravity gradually increases by long-continued ignition, until it attains that of rutile. In the same way the modifications of titanic acid which occur in nature, anatase and brookite, may be converted by continued ignition into rutile. I thought that the publication of these facts would have induced chemists to examine the specific gravity of other oxides at different temperatures, since these changes have an important influence on the atomic volume. This however has not happened, with the exception of a very interesting investigation of Count Schafgotsch, on the specific gravity of silicic acid, in which he has shown that opal heated to redness has so low a specific gravity, that it floats on oil of vitriol; but that the specific gravity is so increased by heating to redness, that it equals that of chemically-prepared silicic acid (2.2), but which is still considerably lighter than quartz and rock-crystal (2.6).

The changes which the three metallic acids under consideration experience by heating to redness are far more remarkable. When the hydrate of pelopic acid is deprived of its water by a gentle red heat over a spirit-lamp, just sufficient to produce the phænomenon of incandescence, and then exposed to a strong red heat in a charcoal fire, its specific gravity is considerably increased. If we examine the ignited acid under the microscope, we see that it consists for the greater part of amorphous granules, in which some small The ignited acid was then exposed to the crystals are perceptible. most intense, and at the same time continuous heat that a platinum crucible is capable of bearing, that of the porcelain furnace of the Royal Berlin Manufactory. The acid was not melted by it, but was converted into a coarse sandy powder, which, examined under the microscope, consisted of large perfect crystals. The specific gravity of the acid however was thereby considerably diminished; curious enough, it had become still lower than that which the acid possessed after the hydrate had been exposed to a gentle heat over a spirit-lamp in order to expel its water.

On repeating this experiment, the specific gravity of the crystallized acid, which had been ignited in the porcelain furnace, was found to be constant, while by no other temperature could the acid be brought to a constant specific gravity.

These experiments are in so far remarkable as they prove precisely the contrary of what has hitherto been frequently admitted. Crystalline bodies, such as vesuvian, epidote and garnet, fuse at a high temperature, become amorphous, but of lower specific gravity. It is evident that what applies to these substances cannot be advanced as a general rule.

Niobic acid has a far lower specific gravity than pelopic acid. It exhibits a similar behaviour. The acid, exposed to the temperature of the porcelain furnace, appears under the microscope perfectly crystalline.

Tantalic acid behaves very different to the other two acids. It is the heaviest of all, and, by heating to redness in a charcoal fire, increases considerably in specific gravity, from 7.0 or 7.1 to 8.2. In the fire of the porcelain furnace it is likewise converted into a coarse powder, but which does not appear distinctly crystalline under the microscope. Its specific gravity is thereby only slightly lessened.

In all these experiments no alteration in the absolute weight was perceptible.—*From the Chemical Gazette* for September 15, 1846.