

Preliminary Note on a New Element allied to Molybdenum.

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Introduction.

In the course of an examination of molybdenite in connection with my work on nipponium, a substance, which was supposed to be ammonium vanadate, was obtained and set aside as such (This Volume, Art. 15, p. 7). A further examination of this substance has shown, however, that it is not ammonium vanadate, but that it is a compound of a new element, closely allied to molybdenum and, indeed, associated with it in this compound; and, although the results so far obtained are still very incomplete, they are now published in the hope that they may prove of sufficient interest.

It is possible and even likely that the "new tin-group element in thorianite", an account of which has been recently given by Miss EVANS (J. C. S., 1908, 93, 666), is identical with this element, inasmuch as the latter has been found not only in molybdenite but also in thorianite and two, at least, of the very few characteristic reactions ascribed to her element by Miss EVANS, namely the formation of a brown sulphide, insoluble in

hydrochloric acid but soluble in hot nitric acid, and its solubility in ammonium carbonate to form a deep brown solution, are likewise produced by the element now to be described. The formation of a golden-brown syrup on evaporation of a nitric acid solution of the sulphide, which she appears to regard as another characteristic of her element, could, however, in the case of the element forming the subject of this paper, be observed only with the impure sulphide, which, in some form or other, was found to contain a small quantity of iron, besides, perhaps, some other elements. Again, on reducing with hydrogen, the oxide prepared from such sulphide, produced a metal, which, in agreement with Miss EVANS' observation, was fusible at a bright red heat, but the metal obtained from the purified oxide was found to be non-fusible. It appears, therefore, that, if Miss EVANS' element is really identical with mine, I have got it in a much purer state. In any case, it is unfortunate that, in consequence of her account being much too short, no exact comparison can be instituted between the two. It is also unfortunate that, in spite of her positive statement as to the existence of molybdenum in thorianite, she does not tell us how this element has been completely removed, the sulphide of molybdenum also dissolving in ammonium carbonate to form a deep brown solution.

There is one other point, which should be noted before going further. Miss EVANS says that the sulphide of her element is soluble in water. The solubility of the sulphide, upon which I worked, may be inferred from the fact that one of its sources was the sulphide residue from thorianite, which had escaped precipitation by hydrogen sulphide (p. 10), and also from the fact that a solution of the purified oxide in ammonia was almost completely precipitated by hydrogen sulphide, *only*

after acidification and *on boiling*. The presence of the element in the filtrate from the hydrogen sulphide group may, therefore, be most probably ascribed to the incomplete heating during precipitation by hydrogen sulphide.

Preparation from Molybdenite of a Compound containing the New Element and its Examination.

As the condition, under which the supposed ammonium vanadate was previously obtained, was such that it did not ensure its separation quantitatively and in the pure state, supposing it to be really ammonium vanadate, the following procedure has been adopted. After igniting in oxygen, the powdered mineral was extracted with ammonia. The residue, still containing some unaltered mineral, was repeatedly boiled with concentrated nitric acid, and the whole evaporated to dryness and again extracted with ammonia. The final residue, on digestion with ammonium sulphide, gave a deep reddish brown solution, which was filtered from the insoluble portion, containing the sulphides of lead, bismuth (?), iron, niobium and zinc, and the hydroxide of aluminium. The dark brown precipitate, obtained on acidifying the solution with hydrochloric acid and heating, was decomposed with nitric acid, and the yellowish brown syrupy residue, left on evaporation of the nitric acid solution, ignited in the air. The dark brown residue thus obtained was fused with potassium nitrate, and the fused mass extracted with water, when a small quantity of a reddish brown substance, consisting chiefly of ferric oxide, was left undissolved. The aqueous alkaline extract was neutralised with nitric acid and, after concentration, mixed with an equal volume of a saturated solution of ammonium chloride,

followed by the addition of one-third of the total volume of 90% alcohol. A crystalline precipitate, apparently the same as that, which had been previously obtained and set aside as ammonium vanadate, was produced on standing for some time, and this was washed, first, with a saturated solution of ammonium chloride and, then, with dilute alcohol.

Judging from the mode of procedure, no other known substance but ammonium vanadate could have come down as a crystalline precipitate under the conditions above detailed, but the reactions described below clearly show that it is not ammonium vanadate. Neither can it be ammonium molybdate, for this salt is not known to be precipitated by ammonium chloride. It is true that the compound gives some of the reactions of molybdenum, which it undoubtedly contains in one form or another, but the fact above alluded to that it has been obtained under conditions, which exclude the possibility of ammonium molybdate being precipitated pure and simple, makes it exceedingly probable either that the compound above obtained is a complex salt containing molybdenum and the new element or that it belongs to the class of mixed crystals.

The yield of the compound was about 7 grams from 400 grams of molybdenite. It is remarkable that the existence, in this mineral, of such a comparatively large amount of a new element should have hitherto escaped observation, but this may be explained by the fact that the element is very closely allied to molybdenum and that its equivalent weight does not differ much from that of the latter.

Properties of the compound. The compound, above obtained, which is evidently an ammonium salt, crystallises in minute

prisms, easily soluble in water; and its aqueous solution gave the following reactions:

(1) Hydrogen sulphide, in presence of hydrochloric acid, only gave a brown colouration without producing any precipitate, but, on heating the solution to boiling, a dark brown precipitate was formed (difference from a vanadate, which is not precipitated by hydrogen sulphide either in the cold or when heated), the filtrate from it being quite colourless (difference from a molybdate, which gives a blue coloured filtrate).

(2) On reducing the solution with zinc and hydrochloric acid, no colour appeared for some time, but, on standing, a blue colour changing to brown was produced; at the same time, a substance having a metallic lustre adhered to the zinc. A solution of pure ammonium molybdate of the same concentration similarly treated at once turned blue, ultimately changing to brown, and the brown solution, on long standing, deposited a dirty brown amorphous substance.

(3) Barium chloride, lead acetate, silver nitrate and mercurous nitrate all gave precipitates, soluble in nitric acid and similar in appearance to the respective salts of molybdic acid, except the mercurous salt. The barium salt forms a white crystalline powder, slightly soluble in water; the lead salt is a white amorphous powder, insoluble in water; the silver salt forms a pale yellow precipitate, slightly soluble in water; and the mercurous salt consists of golden yellow crystals, insoluble in water. Mercurous molybdate is obtained, under like conditions, as a white or pale yellow amorphous substance.¹⁾

1) Struve has observed that the milky precipitate of mercurous molybdate changes into golden yellow needles through prolonged washing or on standing (Journ. prak. Chem., 61, 467, quoted in Dammer's Handbuch der anorg. Chem., II, I 628).

(4) After strongly acidifying the solution with nitric acid, sodium phosphate gave a compound apparently similar to ammonium phospho-molybdate.

(5) In presence of potassium thiocyanate, zinc and hydrochloric acid gave a blood red colouration.

Besides the above described reactions, which were observed with an aqueous solution of the salt, the following must also be mentioned.

(6) The residue, obtained on heating the ammonium salt and consisting of the oxide, either alone or mixed with molybdenum trioxide, did not possess the characteristic yellowish red colour of vanadium pentoxide, but was similar in appearance to molybdenum trioxide and slowly volatilised at a red heat, becoming crystalline at the same time. It produced a deep blue colouration on heating with concentrated sulphuric acid.

(7) The oxide, when heated in a current of hydrogen gas, was reduced into the metal, which was non-fusible at a bright red heat, and the metal could be easily brought back into the oxide by heating it in the air. The equivalent weight of the metal was determined, both by reducing the oxide into the metal and by converting the metal back into the oxide; the values obtained were 16.4 and 16.6, not very far from the equivalent weight of molybdenum.

Thinking that the ammonium salt above obtained might be a mixture of two salts, one containing molybdenum and the other the unknown element, an attempt was made to separate them, if possible, by fractional crystallisation. For this purpose, the salt was again prepared according to the method already described, collecting, however, one crop of crystals shortly after the addition of ammonium chloride and without using alcohol, and another

crop after adding alcohol to the mother liquor and allowing it to stand for two days. From these two fractions, which looked exactly alike, water of crystallisation, ammonium oxide and the residual oxide or oxides were determined with practically the same results.

The attempt, which was next made, to prepare the sodium salt resulted in showing the compound nature of the ammonium salt. The oxide, obtained from the ammonium salt, was fused with an equivalent quantity of sodium carbonate, calculated from the equivalent weight already determined on the supposition that the sodium salt would have the composition Na_2XO_4 ; the fused mass was dissolved in water and the solution evaporated, when hygroscopic crystals were obtained. Under a microscope, these were found to consist partly of thin plates and partly of small needles, but, owing to their hygroscopic nature, their mechanical separation was found to be impossible.

Isolation of the element was, at last, effected through the electrolysis of the ammonium salt. On electrolysing an aqueous solution of the ammonium salt at a temperature of 60° – 70° , using a current density of 1 ampere per 100 sq. cm. and a potential difference of 4 volts, a black substance deposited on the cathode. It was found to contain molybdenum, doubtless, as a hydrated sesquioxide, and, on heating it with 2N-hydrochloric acid, the molybdenum compound gradually dissolved away to form a dark brown solution. Treatment with hydrochloric acid was repeated, until the fresh acid was no longer coloured brown. A portion of the residue (hydrated lower oxide of the new element?), which was graphitic in appearance, was boiled with nitric acid, the whole evaporated to dryness and extracted with ammonia. The ammoniacal solution was also evaporated to dryness

and the residue dissolved in water. This aqueous solution gave all the reactions described on page 5-6, with the exception of the colour reactions mentioned in (2), (5) and (6), but these reactions are exactly those which are characteristic of molybdenum. It is true that a faint colouration was produced with zinc and hydrochloric acid, in presence of potassium thiocyanate, but so faint that, considering the delicacy of this colour reaction, we may reasonably believe that almost every trace of molybdenum has been removed and that the new element or, rather, its oxide or the hydrated oxide has been obtained in an almost pure state.

Properties of the element. The supposed new element, obtained by heating the above described graphitic substance in a current of hydrogen gas, has a metallic lustre and looks somewhat like magnesium powder. It burns brilliantly when heated in the air, producing the oxide, a part of which volatilises at the same time. The oxide, when heated in hydrogen gas, reproduces the metal in the form, however, of a gray powder, resembling molybdenum, produced under like conditions. It is non-fusible at a red heat. On prolonged boiling, it dissolves in concentrated hydrochloric acid, producing a faint greenish-yellow solution. In this latter respect, it is distinguished from molybdenum, which is insoluble in the acid. The hydrochloric acid solution, on evaporation to dryness at 100° , gives a white residue of the chloride, soluble in water. This residue, on ignition, becomes difficultly soluble, doubtless, due to its conversion into the oxide or the oxychloride.

The equivalent weight was again determined, using the purified metal. (1) 0.1464 gr. of the metal gave 0.2149 gr. of the oxide, from which the number 17.1 was calculated. (2) 0.2149 gr. of the oxide gave 0.1451 gr. of the metal, which led

to the value 16.7. Of these two results, the lower value, 16.7, which was obtained from the reduction of the oxide, must be regarded as more exact, there being an unavoidable slight loss by volatilisation of the oxide produced, when the metal is heated in the air, however carefully the heating be conducted. The reduction of the oxide can, on the contrary, be carried on with perfect safety, a lower oxide which is non-volatile at full red heat being, apparently, formed during the first stage of the reduction, so that, if the heating is regulated at the beginning, there is no danger of any loss being incurred.

The atomic weight of the element becomes 100, if calculated from the equivalent weight on the supposition that it is hexavalent, like molybdenum. But the number 100 is that already given to nipponium as its atomic weight (This Volume, Art. 15, p. 19), and nipponium differs from the element now under consideration in its oxide not being reducible by hydrogen, and in other respects. It is possible that nipponium, instead of being divalent, as was supposed, may prove to be a trivalent element, with an atomic weight of 150, but discussion on this point, as well as on the atomic weight of the new element, will be reserved, until the specific heat determinations of the two elements, now being undertaken by Prof. IKEDA of the Science College, and my analyses of their different compounds shall have been completed.

It may be here stated, by way of parenthesis, that a new rich source of nipponium has been discovered. On carefully examining samples of thorianite, there have been found, here and there, small, translucent, prismatic crystals, varying in colour from yellow to red. They are very hard and can scratch glass quite easily. The specific gravity of the mineral is 4.5, being

about one-half of that of thorianite. This mineral was once thought to be zircon, but, on further examination, it has been found that it is a double silicate of zirconium and nipponium, and about 50 grs. of it have been picked out from 5 kilograms of thorianite. It is hoped that several grams of nipponium may now be obtained from this source, about a gram of the metal having been already prepared by the electrolysis of the double fluoride of nipponium and potassium.

Examination of the Sulphide Residue from Thorianite.

While in University College, London, Sir WILLIAM RAMSAY gave me for investigation 1½ kilograms of crude hydrogen sulphide precipitate obtained from 5 cwt. of thorianite. This was ignited, in the air, fused with hydrogen potassium sulphate, extracted with water and reprecipitated by hydrogen sulphide. The filtrate from the precipitated sulphides was treated as in the ordinary course of analysis, and the solution, after the iron-group precipitate had been removed, had a deep reddish brown colour. It did not, however, produce any precipitate with ammonium sulphide, but the colour was suspected to be due to the presence of an unknown element. The sulphur, separated out from the solution on the addition of hydrochloric acid after ammonium sulphide had been added, was found to possess a deep brown colour and to leave a brown residue on ignition. About 100 grams of this sulphur have been brought with me to Japan, and recently examined with the following results.

On ignition, the sulphur gave about 8 per cent of the residue. This was repeatedly extracted with hot concentrated nitric acid, and it was found that the first portions of the extract

had a bluish green, and the later portions a reddish brown colour. Treatment with nitric acid was continued, until no more colour was imparted to it, but a considerable fraction of the brown residue was still left undissolved.

The colour of the first portions of the extract was somewhat like that of a cupric salt, but that it was not due to the presence of this element was shown by the fact that the dark brown—almost black—precipitate produced by sodium sulphide, after nitric acid had been evaporated off, was completely dissolved by an excess of the reagent. The sulphide, reprecipitated from the solution on the addition of hydrochloric acid, was moistened with concentrated nitric acid and ignited, and then fused with potassium nitrate. The brown residue, left on extracting the fused mass with water, was found to consist of an unknown oxide, mixed with ferric oxide, it being this unknown oxide which dissolves in nitric acid with a bluish green colour. The aqueous extract did not contain any molybdenum, but it did contain the same new element as occurs in molybdenite, forming the subject of the present paper, as was shown by the formation of a brown sulphide, soluble in ammonium carbonate to form a deep brown solution, the precipitation of the salts of barium, lead and silver, and, more especially, of the characteristic mercurous salt, as well as by the volatility and the crystalline nature of the oxide obtained from it.

The later portions of the nitric acid extract, which had a reddish brown colour, were evaporated to dryness, when a deliquescent, gummy mass of a brown colour was left behind. On ignition and subsequent fusion with potassium nitrate, it was found to be resolved into the same three constituents as were obtained from the first portions of the nitric acid extract, namely

ferric oxide and the unknown oxide in the residue, after extracting the fused mass with water, this unknown oxide dissolving in nitric acid to form a bluish green solution, and the oxide of the new element in the aqueous extract. It must be here remarked that, although the nitric acid extracts, both green and brown, undeniably contain iron, as is shown by their subsequent treatment, they give no reactions with potassium ferrocyanide.

With regard to the unknown oxide, which dissolves in nitric acid with a bluish green colour, above referred to, no further observation has been made than that it is radioactive, and it is likely that the radioactivity of the sulphide residue from thorianite is due to the presence of this substance. It can be definitely stated that it does not contain any uranium. Since the brown coloured nitric acid extracts also give the same unknown oxide, dissolving in nitric acid with a bluish green colour, after fusion with potassium nitrate, it is possible that the difference in colour may be due to the existence of two different oxides of one and the same unknown element.

Conclusions.

1. Both molybdenite and thorianite contain a new element, which is closely allied to molybdenum.
2. It forms a complex salt (?) with ammonium molybdate, precipitable, from its aqueous solution, in a crystalline form on saturation with ammonium chloride.
3. It appears to form two different oxides, the higher oxide being similar in its properties to molybdenum trioxide and acting as an acidic oxide. The salts of barium, lead and silver, formed

from the higher oxide, resemble the corresponding molybdates, but the mercurous salt consists of golden yellow crystals.

4. The hydrated lower oxide (?) has a graphitic appearance and is insoluble in hot, dilute hydrochloric acid.

5. On heating in a current of hydrogen gas, either of the oxides produces the metal, which is non-fusible at a red heat. It burns brilliantly in the air, producing the higher oxide.

6. The equivalent weight of the metal is somewhat above that of molybdenum, being about 16.7.

7. In producing a brown sulphide and in other respects, above referred to, the new element resembles molybdenum, but is distinguished from the latter in producing no colour reactions, when a soluble salt of its higher oxide is reduced with zinc and hydrochloric acid, either in the presence or absence of potassium thiocyanate, and also by the fact that the metal dissolves in hot, concentrated hydrochloric acid.

8. The "new tin-group element", recently described by Miss EVANS is probably identical with the element, forming the subject of this paper.

9. A new rich source of nipponium has been discovered and, incidentally, described.

10. Besides nipponium and the new element now under consideration, thorianite appears to contain still another new element, the oxide of which is radioactive and dissolves in nitric acid to form a bluish green solution.

