

On the Purification and Testing of Selenion.

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In 1895 I was enabled by a Royal Society grant to obtain about 100 lbs. weight of selenion of about 99·5-per-cent. selenion content. The grant was applied for to enable me to extend to selenion the investigations already made on purified sulphur.* For the purpose of the investigation it was necessary to purify the selenion beyond the standard usual for material to be used in atomic weight investigations. This proved in the event to be impossible on account of the comparatively slight volatility of selenion dioxide, and the impossibility of preventing its formation in the course of the electric measurements I proposed to carry out. Meanwhile, I had prepared a great deal of very pure selenion, and began to investigate its properties—other than those of conduction, for which absolute purity is essential.†

The method of purification adopted was essentially that of Ekman and Petterson.‡

The operations for the purification, as carried out by these chemists, are as follows:—

1. Solution of crude selenion in nitric acid.
2. Expulsion of excess of acid.
3. Sublimation of selenious oxide.
4. Solution of the sublimate in water and filtration (to get rid of the very insoluble mercury selenite).
5. Precipitation of selenion by reduction with hydrochloric acid and sulphur dioxide.
6. Prolonged washing of the precipitated selenion.
7. Reconversion of the selenion into selenious oxide and repeated sublimation in a current of air (to remove possible traces of tellurium).

In addition to a repetition of the above processes, I have investigated the analytical possibilities of the separation of tellurium from selenion, the application of the spectroscope to the testing of selenion for tellurium, the separation of the elements by sublimation of selenion dioxide, and examination of the product.

* Threlfall and Brearley, 'Phil. Trans.,' A, 1896.

† 'Phil. Mag.,' Series 5, p. 42, 1896; 'Phys. Review,' vols. 4 and 5, 1897.

‡ "Über das Atomgewicht des Selens," 'Nova Acta der K. Soc. der Wissenschaften zu Upsala,' May 13, 1876, vol. 10, unpagcd.

The first step was to investigate the original material for tellurium and, if possible, to find a method of detecting that element in small quantities in presence of selenion. The best of the methods I tried was Oppenheim's.* By control experiments it was found that the limits of discrimination lay somewhere between 1/10 per cent. and 1/40 per cent. of tellurium in the selenion—and this only when every precaution is taken. In some trials I used over 40 grammes weight of the original selenion in order to have the advantage of concentration of tellurium. The net result, however, was only to show that there was certainly less than 1/10 per cent. Te, and probably less than 1/40 per cent. I, therefore, in the first instance, tried to obtain a spectroscopic method of detecting tellurium in presence of selenion, and for that purpose experimented with the electric arc, sparking between carbon terminals kept wet with solutions of tellurous acid and tellurium salts, bunsen flames, etc., but in the end failed to find any line of sufficient persistence to be of service. By mixing 99 parts of very pure selenion with one part of tellurium, I failed to obtain any indication of tellurium, no matter what method I employed.

Attempts were made to separate the dioxides of selenion and tellurium by taking advantage of the great difference of solubility of the oxides; the results for small proportions of tellurium showed that a sharp separation could not be effected in this way.

Attempts to take advantage of the difference in the volatility of the oxides as practised by Ekman and Petterson were more favourable, and the results obtained indicated that a sharp separation could be made by one or at most two sublimations at 360° C.

The method was tested by mixing together 10·0098 grammes of selenion, not specially purified, and 0·09985 gramme of tellurium (bought as pure). This mixture was dissolved in nitric acid, evaporated to dryness as usual, and the residue collected and placed in a platinum boat in a wide glass tube. The tube was kept at a dull red heat, and a stream of dried and filtered air was passed slowly over it. The sublimate was then resublimed at from 290° to 320° C. to a spot further along the tube, and it was found that the resublimation of the first sublimate was complete, showing that nothing had been carried forward mechanically. During this process a trace of red selenion was formed—a thing which Ekman and Petterson have shown is not to be avoided, whatever care in eliminating dust may be taken. The second sublimate was dissolved in water and the solution filtered (though it was practically clear), boiled with hydrochloric acid, saturated with sodium bisulphite and left to stand for 15 hours. The precipitated elements were

* Crookes, 'Select Methods of Chemical Analysis,' 3rd edit., p. 422.

washed, ground, and rewashed, and finally treated by the Oppenheim method of separation. This showed that no tellurium was present within the limits mentioned. The residue in the boat containing the metallic impurities was treated for the recovery of tellurium, and 0.0975 gramme of tellurium was recovered and weighed. The loss of tellurium from all causes in this rather complicated treatment was therefore 0.00233 gramme. Taking everything into consideration, this loss appeared to be within the limits of the experimental error. The important fact was that the oxide of selenion sublimed at the lowest visible red heat was totally resublimed at a temperature below 320° without any visible residue being left behind. So far as analysis can show, therefore, it appears that sublimation of the oxides affords a method of separation of the elements—though it cannot, of course, be a theoretically perfect method, for the oxide of tellurium must have some vapour pressure at 300° C.

Preparation of Purified Selenion.

Quantities of 335 grammes of bought selenion were treated in each operation.

The material, ground to a fairly fine powder and sieved, was dissolved in nitric acid, the acid removed, and the aqueous solution of selenious acid filtered. The filtrate was evaporated to dryness and the oxide sublimed in dry and dust-free air at 360° C. To effect the sublimation, the oxide of selenion was introduced into a 3-cm. tube in a large platinum boat and sublimation proceeded with till the tube got blocked up. The boat was then withdrawn, and the sublimate washed out of the tube by platinum distilled water. The air was filtered through long tubes containing cotton wool and dried, first by calcium chloride, and then by pure strong sulphuric acid. During the sublimation a certain amount of reduction always took place at first—while traces of water were being given off and an evil-smelling gas (H_2Se ?) was evolved in small quantity. On resubliming a portion of the sublimate, there was no further reduction or evolution of gas.

The sublimed selenion dioxide was dissolved to an almost absolutely clear and colourless solution in platinum distilled water, and this was then filtered and boiled with much water containing one-ninth of its volume of strong hydrochloric acid, and the selenion precipitated at the air temperature by sulphur dioxide which had passed through several wash bottles and finally through a solution of silver nitrate. Sulphur dioxide was at first prepared from copper and sulphuric acid, and though there was no milkiness in the wash bottles or darkening of the precipitated silver sulphite, it was feared that some sulphuretted hydrogen might possibly be formed, and therefore

recourse was had, first to the production of the gas from sodium bisulphite, and finally to its production from the combustion of very pure sulphur. In the latter case rather elaborate arrangements were required. The sulphur was burned in a large sheet-iron cylindrical vessel, provided with a zinc tray containing the sulphur. The gases coming from the chamber passed in order through a glass tube 7 feet long; a plug of glass wool, a Liebig's condenser, Woolfe's bottle containing distilled water, a plug of cotton wool 2 inches long, a tube containing more cotton wool and copper turnings; a tight plug of glass wool (to filter off the dust from the cotton wool if any was produced), and a long tube containing copper and silver foil. The precipitation vessel was closed and communicated with a suction pump, whereby the gases were drawn through the system. Most of the selenion prepared was precipitated by sulphur dioxide, prepared as described.

The operation of precipitating selenion is not complete for some time. The fine red powder of selenion (which is free from lumps or coagulated portions when the precipitation has been carried out without appreciable rise of temperature) was washed on a platinum cone, and then exhibits many of the characteristics of a gelatinous substance—for instance, it could be got to vibrate when distorted, just like a jelly.

The washing is continued till some time after no trace of hydrochloric or sulphuric acid can be detected in the washings. The fine selenion is then coagulated to some extent by starting the filtering pump, which causes it to occupy a much reduced volume, and finally dried in a dish in a water bath, when a great deal of water separates and the selenion coagulates and becomes dark in colour. No HCl or H_2SO_4 could be found in the water which separated.

The drying is continued till the mass can be broken up, when it is again heated in a water oven and finally placed in a vacuum desiccator.

When the selenion appeared to be dry, it was distilled in a current of air residue in a hard glass retort protected by a fireclay and asbestos coating.

The air residue, consisting for the most part of nitrogen, was produced as described in a previous paper.*

In spite of all precautions, some oxide of selenion appeared in the receiver, and this was as far as possible caused to deposit on the top of the receiver by keeping the selenion hot, but of course there is no certainty that it was all concentrated there.

An attempt was made to get rid of SeO_2 by redistilling the selenion from bulb to bulb *in vacuo* in a tube blown with three bulbs. The first bulb was charged with some of the distilled selenion which had come over first, the

* 'Phil. Mag.,' Series 5, vol. 35, p. 1, Jan., 1893.

tube was pumped out by a Sprengel pump and filled with the air residue, and was also provided with a piece of metallic magnesium at one end. The magnesium was heated both during pumping and later, when the tube was sealed off. The tube was heated while still in connection with the pump, and as the selenion melted it just gave enough gas to change the sound of the pump, but not enough to examine—it was estimated at less than $1/20$ of the volume of the selenion (say $1/10$ c.c.). There was sufficient selenion dioxide driven off by heating the selenion to form a visible deposit on the next bulb of the tube. Now the heating may be considered to have taken place under conditions precluding the presence of any appreciable amount of oxygen in the high vacuum attained in presence of hot magnesium, so we must conclude that the selenion, as prepared in bulk, either contains some oxide, or oxidises during removal and storage at ordinary temperatures. Even if it had been practicable to heat all the selenion in a high vacuum, there is no evidence that all the oxide could be separated, and no test can be made to establish with certainty that oxide is absent, even after such treatment (see below). I was therefore obliged to abandon the scheme of treating selenion as a simple elemental body for conductivity experiments.

The selenion, prepared in the manner described above, was tested in the following way—it being recognised that both arsenic and mercury, besides unknown elements, might be present.

Samples of about 10 grammes weight were dissolved in strong nitric acid, the acid evaporated with constant additions of water on the water bath, and the dry selenion dioxide dissolved in water. In all cases the nitric acid solution was absolutely clear and left no residue. The aqueous solution was just visibly opalescent, possibly through a slight reduction of the selenious acid by dust or owing to the presence of mercury selenite.

There appears to be some question as to the reliability of the modern methods of testing for arsenic in presence of selenion.* After some preliminary trials, the following method was adopted.

Ten grammes of selenion were converted into selenious acid and dissolved in water. The solution was mixed with a large excess of a solution of ferrous chloride and distilled in presence of a stream of hydrochloric acid gas bubbled through the apparatus. Water was added till the distillate measured three times the volume of the original mixture put into the retort. The distillates were divided into four portions, of which the first and last were much smaller than the second and third. All distillates were saturated with H_2S with all precautions and filtered. The precipitates (visible or invisible) were dissolved in small quantities of 20-per-cent. solution of pure sodium hydrate, acidified

* Berry, 'Soc. Chem. Ind. Journ.,' 1901, p. 322.

with sulphuric acid, boiled with potassium meta-bisulphite, and used in the electrolytic arsenic apparatus of Dr. Thorpe.*

The first distillate was from the ferrous chloride and hydrochloric acid only, and showed no arsenic, the second and third gave arsenic mirrors, and the fourth no mirror.

The total arsenic collected amounted to 0.05 milligramme As_2O_3 or 0.00038 per cent. arsenic in the material tested.

Check experiments were made to test whether the selenion, in being reduced by the ferrous chloride and hydrochloric acid, prevents arsenic from distilling over, and whether the Thorpe apparatus gives a correct result for a solution of selenide of arsenic when treated as above. The result of these tests was to show that the ferrous chloride distillation is effective in causing the arsenic to pass into the distillate, and that the arsenic is properly shown by the Thorpe apparatus. I have to thank Mr. T. H. Waller for suggesting the distillation with ferrous chloride and hydrochloric acid.

Testing for Mercury.—This is a matter of some difficulty, but the fact that an almost absolutely clear solution of selenious acid was obtained precludes the possibility of the presence of more than very minute quantities. Two methods of testing were employed.

In the first, 10 grammes of selenion were converted into sodium seleniate—or at all events selenious acid was neutralised with sodium hydrate and the product dried. The dry salt was then heated in a tube between plugs of glass wool to a bright red heat in a current of purified and dried air just sufficient to insure that anything capable of subliming should be carried into the cool part of the tube. The result was a large sublimate of selenious oxide. This sublimate was dissolved in water, saturated with excess of precipitated carbonate of calcium, dried on the water bath, and reheated in a hard glass tube, as before, first to a dull and afterwards to a bright red heat. The cold part of the tube contained a just visible sublimate. Mercury was tested for by Marcel's method,† using one strip of paper saturated with ammoniacal silver nitrate, and another saturated with hydrochloroplatinic acid. The paper saturated with the silver compound did darken as the sublimate was chased up to it by a flame, but the appearance was not that produced by mercury, as shown in a check experiment; the platinum paper was not affected. This is a very sensitive test for mercury as claimed by Marcel.

The second investigation was kindly made for me by Dr. H. Sand, of Nottingham, by means of a rotating cathode which he has studied in regard

* 'Chem. Soc. Trans.,' 1903, vol. 83, p. 969.

† 'Comptes Rend.,' 1873.

to the separation of metals by electrolysis at carefully regulated voltages. About 11 grammes of the purified selenion were converted into selenious acid—acidified with nitric acid and electrolysed under the conditions known to precipitate mercury from other salts—on to the rotating cathode. After an hour's work no deposit could be detected on the cathode, so it was made an anode in a small quantity of dilute nitric acid and a current passed to a fine platinum wire cathode. No mercury was deposited on the fine wire.

The sensitiveness of the method has not been communicated to me by Dr. Sand, but it probably is sensitive enough to show the presence of small quantities of mercury. We may conclude that either there is no mercury in the purified selenion, or if there is it is probably of the order of the arsenic content.

A sample of the selenion which had been used by Messrs. Mason and Vonwiller was returned to me for examination towards the end of 1906, and was examined by solution in nitric acid, etc. Nothing large enough to weigh could be extracted from 10-gramme samples, but there was, nevertheless, evidence that the selenion had picked up some impurities in the varied experiments which had been made upon it. Originally it was some of the purified and distilled product described above. There was a trace of organic matter separable from the nitric-acid solution, and a few specks of insoluble white matter in the aqueous solution of selenious acid. There was also a trace of iron and alumina. The result of treating the filtrate from selenion precipitated by hydrochloric acid and sulphur dioxide with sulphuretted hydrogen was a minute dark-coloured precipitate which was tested in the usual way, but could not, owing to its small quantity, be satisfactorily examined. Special tests for gold and platinum showed that it was not the latter, the former doubtful, and it did not appear to be mercury. Taking all the residues and precipitates together, the total weight could not have been more than 1 or 2 milligrammes. My opinion is that the contamination consisted mainly of dust with a trace of mercury or gold, and some hydrocarbon—possibly oil or paraffin.

In letters of October 30 and November 19, Professor Pollock informs me that the selenion was, in fact, floated on mercury in some of the experiments and gilded in others, and the material had been remelted at least a dozen times, so some contamination was to be expected. I made a special investigation for zinc, as Messrs. Mason and Vonwiller state that the selenion was melted in a zinc vessel, but the material was found absolutely free from this element, at all events to tests by potassium ferrocyanide and sodium sulphide, which are fairly delicate.

A test for SeO_2 was made in the following manner: About 4 grammes of the selenion was placed in a hard glass tube 1 cm. diameter, drawn out to a long point—about 20 cm. long and 2 mm. diameter. The tube was connected with an apparatus for supplying hydrogen absolutely freed from oxygen, and was filled and pumped out many times. Finally, the pressure was reduced to about 30 mm. mercury, and sufficient hydrogen allowed to enter to insure that sublimate would be carried into the narrow part of the tube. A just visible sublimate of SeO_2 was observed. On repeating the trial with the same selenion to which 1 milligramme of SeO_2 had been added, the sublimate was, at least, doubled, and, on adding 4 milligrammes, a comparatively large sublimate was obtained, but it was almost instantly covered over by a deposit of selenion, or was reduced and thus removed. I think it is safe to conclude that 4 grammes of the selenion used by Vonwiller and Mason did not contain anything like 5 milligrammes of SeO_2 , and probably only about 1 milligramme; but the test is not entirely satisfactory.

My thanks are due to Dr. George Elliot, of Sydney, for his kindness in supplying me with considerable quantities of specially purified acids.
