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# THE ATOMIC MASS AND DERIVATIVES OF SELENIUM.[1]

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## INTRODUCTION.

THE following contribution to our knowledge of selenium was undertaken with the view of studying the various derivatives and reactions of the element, and using such methods or compounds as would prove available in the determination of its atomic mass.

In the series presented, ratios have been determined in compounds differing widely in character and composition, and by methods entirely unlike in nature.

The action of hydrochloric acid gas upon the salts of acid oxides which possess the power of forming volatile compounds with it, affords a clean and accurate method, which can be used in establishing the atomic ratio.

A salt of such a character, when subjected to the action of the gas, yields a substance removed at once from the field of action, while in the vessel which contained the original salt there remains a chloride which can be directly weighed.

Such a method almost completely eliminates the factor of personal error, in that the operator needs but weigh the original

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[1] Author's thesis for the Degree of Doctor of Philosophy.

salt and the resulting chloride, no manipulation intervening in which he is directly concerned.

If it be possible to use a salt whose resulting chloride can be directly reduced to metal, we have a means of establishing from one salt two series of ratios, which if agreeing, both as individuals and series, means that a ratio has been established comparable to that existing between the metal and its chloride. If two such series agree, a direct proof is established of the purity of material and accuracy of the method.

An ideal salt for such treatment is a salt of silver; first, since its chloride can be directly reduced to metal by heating in a current of hydrogen gas; second, the ratio between silver and chlorine is one of the most firmly established ratios. Silver selenite is an anhydrous salt, which crystallizes well, is unaffected by light, and is perfectly stable. This substance, when treated with gaseous hydrochloric acid, yields silver chloride and a hydroxychloride of selenium, corresponding in composition and properties to that obtained by A. Ditte,[1] when acting on selenium dioxide with hydrochloric acid gas.

In the first series of experiments, silver selenite was weighed, treated with hydrochloric acid gas, and silver chloride formed, which was weighed. In the second series, silver selenite was weighed, converted into silver chloride, which was weighed, the chloride was reduced in hydrogen to metal, and this again weighed; two ratios were thus established from one sample of selenite by comparison with silver and chlorine, and with metallic silver.

A study of all the known double bromides has been made, and new bromides of rubidium and cesium prepared. Of all the salts examined, the one which seems best adapted for the purpose of an atomic mass series is the ammonium salt. This substance is easily obtained pure and crystallizes well. When treated with hydroxylamine, selenium is set free, and the element itself can be brought on an asbestos filter, washed, dried at 100°, and weighed.

The use of hydroxylamine, according to the method of Dr. Harry F. Keller,[2] for the precipitation of selenium, affords the

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[1] *Ann. chim. phys.*, (5), 10. 82.

[2] Private communication from the author.

clean and accurate determination that has long been desired by those who have used the tedious and uncertain precipitation by sulphurous acid or sodium sulphite in hydrochloric acid solution.

In many of the double halides which contain the ammonium group it has been possible to replace the ammonia by organic bases. This is especially the case in many of the salts of the metals of the platinum group. A series of salts has been prepared and studied in which the ammonia in ammonium bromoselenide has been substituted by fatty amines or aromatic bases. It was hoped that it would be possible to find a compound which would be of such character that it could be subjected to careful analysis. Such was not the case; none seemed to meet the demands imposed on them.

Finally a study was made of the monoxide of selenium, the existence of which has been repeatedly questioned.

## FIRST SECTION.

### HISTORICAL.

The atomic mass of selenium has been determined by a number of workers and by various methods. Figures have been obtained which range between 78.52 and 79.35 ($O = 16$).

The first to determine the atomic mass of this element was Berzelius.[1] He found that 100 parts of selenium, when treated with chlorine, gave 179 parts of the tetrachloride. If chlorine be 35.45, the atomic mass of selenium would be 79.22, from the single determination mentioned.

The next work was by Sacc,[2] who presents two series. The first includes three reductions of selenium dioxide with ammonium bisulphite and hydrochloric acid. This series gives selenium the atomic mass 78.68 ($O = 16$). The second series was obtained by treatment of barium selenite with sulphuric acid, and the subsequent weighing of barium sulphate. The mean of the four determinations gave 78.52 ($O = 16$, $S = 32.07$, $Ba = 137.43$).

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[1] Pogg. *Ann.*, **8**, 1.

[2] *Ann. chim. phys.* (3), **21**, 119.

In 1852, Erdmann and Marchand[1] analyzed repeatedly sublimed and well-crystallized selenide of mercury, and obtained the figure 78.83 (Hg = 200) ; a value between that of Berzelius and Sacc.

Eight years later, Dumas[2] repeated the work of Berzelius, passing chlorine over selenium. He obtained the value 79.35 (Cl = 35.45).

In 1876, Ekman and Pettersson ignited silver selenite, metallic silver was obtained, which retained traces of selenium. Their result is 79.00 (Ag = 107.92). They also present a second series in which selenious acid was reduced by sulphur dioxide in the presence of hydrochloric acid. The selenium was brought on a glass filter and weighed. The second series gave a mean of 79.04 (O = 16).

## DETERMINATION OF THE ATOMIC MASS OF SELENIUM BY THE HYDROCHLORIC ACID METHOD.

### PREPARATION OF PURE SILVER BY THE METHOD OF STAS.

About 100 grams of ordinary pure silver were dissolved in hot dilute nitric acid. The solution was evaporated to dryness, the mass heated to the point of fusion, and held at that temperature until the oxides of nitrogen ceased to evolve. The cold residue was dissolved in water and this solution allowed to stand forty-eight hours, when it was run through a double filter to remove any suspended matter. After diluting the filtrate with thirty times its volume of distilled water, an excess of pure hydrochloric acid was added. The silver chloride was allowed to settle, after which it was washed by decantation with water containing a little hydrochloric acid, and finally with pure water. The silver chloride was collected on a cheese-cloth filter, pressed well and allowed to dry. When perfectly dry it was digested with aqua regia for several days, after which it was again washed by decantation with water. The pure silver chloride, thus prepared, was ready for reduction with milk-sugar and caustic potash. It was then necessary to purify the milk-sugar

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[1] *J. prakt. Chem.*, 55, 202.

[2] *Ann. Chem. Pharm.*, 113, 32.

and potassium hydroxide, which were to be used in reducing the chloride to metal. The potassium hydroxide was heated to boiling and treated with a strong solution of potassium sulphide to precipitate any heavy metals which might be present. After filtration, the solution was treated with freshly precipitated silver oxide, and again filtered to remove the excess of potassium sulphide. The milk-sugar which was used was purified in a similar manner. The silver chloride was placed in a large porcelain casserole and covered with a solution of caustic potash and milk-sugar. The dish was exposed to a heat of 70°–80° until complete reduction had taken place. The silver appeared as a gray-white mass. It was washed with distilled water until the washings no longer gave an alkaline reaction, after which it was digested with dilute sulphuric acid, and finally washed with dilute ammonia. The silver thus obtained was mixed with five per cent. of its weight of fused borax and ten per cent. of sodium nitrate. This mixture was fused in a clay crucible. The metal obtained was snow-white in appearance. It was dissolved in nitric acid to a clear solution. This solution was evaporated to dryness and the resulting nitrate was obtained as a pure white mass.

## PREPARATION OF PURE SELENIUM DIOXIDE.

Several hundred grams of quite pure selenium were treated with nitric acid. The resulting selenious acid was evaporated to hard dryness, when the dioxide was formed. This was dissolved in water, filtered through a double filter, hydrochloric acid was added and sulphur dioxide conducted into the warm solution. The selenium thus produced was washed with water, until the washings no longer gave an acid reaction, finally dried and fused. Broken lumps of this material were placed in a crystallizing dish on a water-bath heated to 70°. Pure nitric acid was added to cover the mass, a brisk evolution of nitrous fumes took place, and the selenium was oxidized to selenious acid. When all action appeared to be over, the solution was evaporated to dryness to remove the excess of nitric acid. The residue was dissolved in distilled water, and the solution transferred to a porcelain dish. The solution was then carefully evaporated on an iron plate, and the heat gradually increased until the sublimation point of selenium dioxide (about the boiling-point of sulphuric acid) had been reached. When selenium dioxide began to sublime, a glass funnel, the neck of which had been closed with cotton, was placed over the dish, the base of the funnel resting on the inside of the dish and fitting closely. Selenium dioxide is thus sublimed and collects on the inside of the funnel as white needle-like crystals, often several inches long. The dioxide was resublimed three times. When an attempt is made to sublime selenium dioxide which is slightly impure, red selenium contaminates the otherwise white deposit. Traces of organic matter or other impurities, in slight amount, cause a red coloration, but when pure no reduction takes place during the sublimation. The long white needles were carefully removed from the funnel by means of a platinum spatula, and dissolved in distilled water. To this solution pure barium hydroxide was added until further addition failed to produce a permanent precipitate. Any sulphuric acid that might be present was thus removed along with any selenic acid. The solution containing the barium precipitate was allowed to stand over night, after which it was filtered. The clear solution was evaporated to dryness in a porcelain dish, the residue heated on an iron plate, and finally sublimed into a dry glass funnel as before. The clear needle-like crystals were picked out and resublimed three times. Selenium dioxide thus formed is perfectly stable in dry air, but in the ordinary atmosphere absorbs moisture rather rapidly.

## PREPARATION OF SILVER SELENITE.

Selenium dioxide was dissolved in water, forming selenious acid. To this a solution of pure silver nitrate was added, slightly in excess. A few drops of selenious acid were added, when a complete precipitation of both silver and selenium takes place. The resulting white selenite of silver was thoroughly washed with water by decantation. The water was drained off as completely as possible, and the white mass dried by gentle heat. The powder was treated with pure nitric acid, one part to three parts of water, and heated. On cooling, silver selenite crystallizes from such an acid solution as an anhydrous salt, consisting of flat plates. These plates were broken up, washed well with water, and again treated with dilute nitric acid. The salt was recrystallized three times. Finally the selenite was thoroughly washed with water and dried by heating to 70°–80° in an air-bath for twelve hours. The salt was carefully tested for nitrate and nitric acid, but none were found to be present.

A bottle of the material prepared was allowed to remain in direct light for a period of twelve months, and at the end of that time showed no discoloration.

By comparison of a known weight of the salt with pure benzene, the specific gravity of selenite of silver was found to be 5.9297.

## DESCRIPTION OF APPARATUS.

Hydrochloric acid was prepared by the method which has been found very satisfactory in this laboratory, and consists in evolving the gas by adding concentrated sulphuric acid to concentrated aqueous hydrochloric acid. The hydrochloric acid was contained in a three-liter flask, and sulphuric acid was dropped on it from a separatory funnel. By regulating the current of sulphuric acid with a stop-cock, a constant evolution of gas is obtained at the ordinary temperature. Only pure acids were used, and such being the case, it was sufficient to dry the gas by passing it through two wash-bottles containing concentrated sulphuric acid, and a tower containing broken pieces of anhydrous calcium chloride. The dry gas was conducted through a combustion tube of hard glass, in which was placed a weighed quantity of silver selenite. The posterior portion of the tube was bent and directly connected by means of a stop-cock with a glass bulb containing water.

## CORRECTIONS.

The weights used were carefully calibrated, first by comparison against each other, then against a normal weight. The larger weights were of brass, gold plated, the smaller ones being of platinum. All weights given have been reduced to vacuum. The following formula was used :

$$W = P + P\sigma\left(\frac{1}{\Delta} - \frac{1}{B}\right)$$

Where $P$ = weight of substance,
$\sigma$ = density of the air,
$\Delta$ = specific gravity of the substance,
$B$ = specific gravity of the weights.

The balance used was a short-arm Becker, the sensibility of which was determined to be one-twenty-fifth of a milligram.

### METHOD OF PROCEDURE.

By allowing gaseous hydrochloric acid to come in contact with selenium dioxide, A. Ditte[1] formed $SeO_2.2HCl$. He states that the compound consists of brilliant scales, which at 26° decompose into an amber-colored liquid of the composition $SeO_2.HCl$.

In performing the following experiments, the method of procedure was to weigh a definite amount of silver selenite into a previously weighed porcelain boat, introduce the boat into the combustion tube, and start the current of gas. After allowing the gas to pass over the salt for at least half an hour in the cold, a small flame was brought under the tube, and the boat gently heated. When the gas comes in contact with the selenite, rapid absorption takes place, the salt assuming a yellow color, due to the formation of the hydrochloride. In order to avoid any loss by spattering, as the salt becomes slightly moist, the boat was covered with a piece of platinum foil, and the heat increased very gradually. When it was thought that the selenium dioxide had been completely expelled, the tube was allowed to cool, and the boat removed to a desiccator containing soda-lime. After standing several hours, the silver chloride was weighed, replaced in the combustion tube and the gas conducted over it for one-half hour longer. The tube was again heated, and the chloride brought just to the point of fusion. It was again replaced in the desiccator, allowed to stand several hours, and reweighed. In all cases the weights of the boat before and after this second treatment were the same, a point which seems to indicate that silver chloride sustains no perceptible loss when brought to the point of fusion. The silver chloride was tested for selenium, but none was found.

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[1] *Ann. chim. phys.*, (5), 10, 82.

| $Ag_2SeO_3$. Grams. | AgCl. Grams. | Se. Atomic mass. |
|---|---|---|
| 0.98992 | 0.82715 | 79.326 |
| 1.59912 | 1.33600 | 79.373 |
| 2.70573 | 2.26087 | 79.320 |

Mean = 79.339
Probable error = ±0.011

Having thus demonstrated that hydrochloric acid gas will completely drive out selenium dioxide from silver selenite, leaving behind pure chloride, according to the equation,

$$Ag_2SeO_3 + 4HCl = 2AgCl + SeO_2.2HCl + H_2O,$$

the next step was to reduce the chloride formed by this reaction to metal.

## SECOND SERIES.

Hydrogen gas was generated by the action of dilute sulphuric acid on mossy zinc. The gas was purified by conducting it through a series of wash-bottles; the first containing silver sulphate; the second, potassium permanganate; the third, lead nitrate; and the fourth, caustic potash. It was then dried by passing through sulphuric acid. The pure gas was conducted through a tube of porcelain in which the reduction took place. The excess of hydrogen and the hydrochloric acid formed were passed through a wash-bottle containing sulphuric acid, following which was a wash-bottle containing water to absorb the hydrochloric acid. The unused hydrogen was allowed to escape into the room.

The boat containing the silver chloride, after being weighed for comparison with silver and oxygen, was introduced into the porcelain tube, all connections were closed and a brisk current of hydrogen conducted through the apparatus. When the hydrogen was free from air, the combustion furnace, containing the porcelain tube, was started and the heat gradually increased until the outside of the tube attained bright redness. This temperature was maintained for a period of three hours, when the tube was allowed to partially cool, the boat and its contents were removed to a desiccator. After standing several hours, it was weighed, replaced in the combustion tube, and hydrogen again conducted over it at a red heat for an hour. The boat was again removed to a desiccator, cooled as before, and reweighed.

The weights before and after reignition in hydrogen were in all cases the same. After the last weighing, the boat and contents were treated with pure dilute nitric acid and warmed. Complete solution ensued, showing the reduction of silver chloride to metallic silver had been complete. Tests were made for selenium in the resulting solution, but none was found.

| $Ag_2SeO_3$. Grams. | AgCl. Grams. | Se. Atomic mass. | Ag. Grams. | Se. Atomic mass. |
|---|---|---|---|---|
| 0.26204 | 0.21897 | 79.299 | 0.16480 | 79.356 |
| 0.58078 | 0.48522 | 79.371 | 0.36534 | 79.280 |
| 0.70614 | 0.58999 | 79.350 | 0.44417 | 79.301 |
| 0.80811 | 0.67532 | 79.282 | 0.50821 | 79.369 |
| 0.98396 | 0.82232 | 79.263 | 0.61882 | 79.358 |
| 1.29685 | 1.08350 | 79.361 | 0.81562 | 79.277 |
| 1.63103 | 1.36288 | 79.316 | 1.02588 | 79.320 |
| 2.00162 | 1.67234 | 79.358 | 1.25884 | 79.357 |
|  |  | Mean 79.325 |  | Mean 79.329 |
|  |  | Probable error ±0.009 |  | Probable error ±0.009 |

## EXPERIMENTS WITH SODIUM SELENITE.

In order to ascertain if the alkaline selenites would prove as well adapted for treatment with hydrochloric acid gas as the silver salt, a study was made of sodium selenite.

Sodium carbonate was purified by recrystallization several times. It was found, when tested, to be free from sulphate, chloride, and silicate. The salt was fused in a platinum crucible under a blast-lamp. Equivalent weights of the carbonate and selenium dioxide were dissolved in water, the solutions combined and evaporated to dryness. The salt obtained was recrystallized seven times from water. Crystallization takes place only when the liquid has attained the consistency of a thick sirup. The salt obtained in this manner, when treated with dilute hydrochloric acid, showed the presence of a slight amount of carbonate, hence was rejected.

An attempt was made to prepare the sodium salt by ignition of the acid selenite. In this case, a salt of constant composition could not be obtained. At a temperature slightly above that of complete conversion into neutral selenite, the salt appears to lose slight amounts of selenium dioxide, varying with the temperature.

# DETERMINATION OF THE ATOMIC MASS OF SELENIUM BY ANALYSIS OF AMMONIUM BROMOSELENATE.

In the following part, devoted to the double bromides, a study has been made of a large number of derivatives. It is sufficient to state here that the salt found most suitable for careful analysis is the double bromide of ammonium and selenium. A description of the properties of the salt is entered into more fully in Section II.

## PREPARATION OF PURE BROMINE.

Bromine was purified by distillation over manganese dioxide and concentrated sulphuric acid. A retort containing this mixture was heated on a water-bath and the distillate collected in a chilled receiver. This product was brought in contact with manganese dioxide and again distilled. Having started with pure bromine of commerce, chlorine and organic matter would, if present, be eliminated by this procedure.

## AMMONIUM BROMIDE.

So-called "pure" ammonium bromide was twice recrystallized, the crystals dried each time by pressing between pieces of filter-paper. It was then twice sublimed and again crystallized. The salt was allowed to remain for several days in a desiccator to become thoroughly dry. Thus obtained, ammonium bromide is pure white, dissolves in water to a clear colorless solution, and on ignition leaves no residue.

## SELENIUM.

Selenium dioxide, purified in the manner previously described, was dissolved in water containing hydrochloric acid. Sulphur dioxide, generated by the action of sulphuric acid on copper turnings, was washed by sulphuric acid and conducted into the warm solution. Selenium was precipitated. It was washed with hot water until the washings no longer gave an acid reaction. After drying it was fused to the black glassy modification. While yet liquid, the mass was poured from the crucible in which it had been fused, on a porcelain plate, allowed to cool, and finally broken into small fragments.

### AMMONIUM BROMOSELENATE.

Nine and eight-tenths parts of ammonium bromide were dissolved in water; to this solution four parts of selenium were added, bromine was introduced till in slight excess, and perfect solution had ensued. The solution of ammonium salt was brought on a water-bath, the excess of bromine expelled and allowed to slowly evaporate, when ammonium bromoselenate separated. The crystals were removed from the mother-liquor, dried by pressing between filter-paper, dissolved in water containing hydrobromic acid, which had been repeatedly distilled, and allowed to crystallize at the temperature of a water-bath. The crystallization was repeated several times. Finally, the salt was placed in a desiccator containing soda-lime where it remained several days. Examined under the microscope, the red crystals showed no admixture of ammonium bromide. The specific gravity of the salt was determined in benzene and found to be 3.3266.

### METHOD OF PROCEDURE.

A weighed quantity of the salt is dissolved in water, and to this is added a few cc. of ammonia. Pure hydroxylamine hydrochloride is introduced in slight excess, when a reaction takes place, probably as expressed in the following equation:

$$SeO_2 + 6NH_2OH = Se + 2NH_3 + 6H_2O + 2N_2O.$$

Selenium appears in the cold as a flocculent red precipitate. The solution is gradually warmed to expel free ammonia, and render the solution neutral. Under the influence of heat the precipitated selenium changes to the gray variety. The precipitate is brought upon asbestos felt, prepared by pouring asbestos suspended in water into a Gooch crucible, and sucking hard and dry by means of a good filter-pump. This filter, having been ignited and weighed, the solution containing the selenium is poured upon it, the selenium washed thoroughly with hot water, dried for two hours in an air-bath heated to 100°, and allowed to cool in a desiccator. The increase in weight of the crucible represents the selenium in the original salt. All of the filtrates were preserved, evaporated together, and tested for selenium, but none could be detected, showing the precipitation was complete.

| $(NH_4)_2SeBr_6$. Grams. | Se. Gram. | Se. Atomic mass. |
|---|---|---|
| 1.00059 | 0.13324 | 79.243 |
| 1.50153 | 0.20022 | 79.367 |
| 2.00059 | 0.26649 | 79.273 |
| 2.00126 | 0.26657 | 79.269 |
| 3.00125 | 0.39958 | 70.226 |
| 4.00216 | 0.53346 | 79.333 |
| 5.00218 | 0.66656 | 79.306 |
| 5.03001 | 0.66998 | 79.267 |
| | Mean | 79.285 |
| | Probable error = | ±0.011 |

Mean from silver chloride, 79.329 (11 determinations).
Mean from metallic silver, 79.329 ( 8 " ).
Mean from analysis of ammonium bromoselenate, 79.285 ( 8 " ).
Giving a general mean, 79.314

The values used in calculation are those given by Clarke (Atomic Weights, 1897), and are as follows :

| | |
|---|---|
| Ag | 107.92 |
| Br | 79.95 |
| Cl | 35.45 |
| O | 16.00 |
| N | 14.04 |
| H | 1.008 |

The mean of all determinations is close to the values obtained in the synthesis of selenium chloride being slightly higher than the determination by Berzelius and a trifle lower than the series of Dumas.

From selenite of silver values are presented from quantities, the greatest of which is ten times the least, the difference in the ratio obtained in these extremes being but slight. In the series obtained from ammonium selenium bromoselenate, the maximum quantity used is five times that of the minimum.

That the mean of the series from silver selenite approaches very closely the true atomic mass of selenium, can be little doubted. The values obtained in the reduction of silver chloride to metal express the commonly accepted ratio between silver and chlorine.

Selenium was shown to be completely removed from silver selenite by hydrochloric acid, and complete reduction of silver chloride to metal was proved in every instance. These facts seem to afford good proof of the reliability of the hydrochloric acid method and the subsequent reduction process.

The advantages this method possesses over those used by previous workers is, first, the great reduction of the factor of personal error, in that the only part in which the operator is directly concerned is the weighing of material and product; second, the establishment, from one weight of starting material, of two values, whose mutual agreement depends on their similarity to a well-established ratio. The latter point indicates that the ratios prove themselves.

Additional evidence that the atomic mass of selenium is very close to the value given by the silver salt is furnished by the analysis of ammonium bromoselenate. This latter salt is easily obtained pure, and by decomposition with a reducing agent such as hydroxylamine, selenium itself can be weighed. In contrast to the previous method, the manipulation of the operator must needs play a great part, yet the satisfactory precipitation of selenium by hydroxylamine seems to be a strong point in its favor.

## SECOND SECTION.

### INVESTIGATION OF THE DOUBLE BROMIDES.

Considerable attention has been drawn to the double bromides of tellurium by Wheeler.[1] Earlier work was done in the same line by Berzelius,[2] Rammelsberg,[3] and von Hauer.[4] Little was done on the corresponding derivatives of selenium, until Muthmann and Schäfer[5] prepared the double bromides of selenium with potassium and ammonium. The chlorides have received but little attention, and from what little has been done, they are known to be difficult to prepare. The double bromides are well-defined crystalline salts. The combination which takes place between selenium tetrabromide and certain of the alkaline bromides is so definite as to lead to the view that they are salts

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[1] *Am. J. Sci.*, [3], **45**, 267.

[2] Pogg. *Ann.*, **32**, 577.

[3] *Ber. Monats. Ber.*, *1875*, 379.

[4] *J. prakt. Chem.*, **73**, 98.

[5] *Ber. d. chem. Ges.*, **26**, 1008.

of hydrobromoselenic acid. Like the tellurium salts, they follow but one type, $Me_2SeBr_6$.

By examining these double salts, it was thought one or more might be found, which would answer the requirements of a starting material for the determination of the atomic mass of selenium. To this end a study has been made of the inorganic salts, and a number containing organic groups have also been prepared. Of all the salts examined, the most satisfactory one was the ammonium salt. The pyridine derivative appears as beautiful red scales, but the fact that it is only possible to obtain the salt from alcoholic solution, and that it is likely to suffer secondary decompositions, seemed to be an objection to its use in accurate analysis.

The method Muthmann and Schäfer employed in the preparation of the bromoselenates of potassium and ammonium was to treat selenium dioxide with hydrobromic acid, when a solution of selenium tetrabromide was formed. To this they added a saturated solution of potassium or ammonium bromide, and boiled. On cooling, a dark orange red powder separated, which contained octahedral crystals of bromoselenate.

A simpler and more convenient method of procedure was found to consist in adding bromine directly to a solution of the alkaline bromide, in which had been introduced the amount of selenium requisite to form the desired bromoselenate. The reactions took place in the following manner: Bromine coming in contact with selenium formed a dark layer of liquid monobromide, which being heavier than the solution, remained at the bottom of the vessel. Further addition of bromine converted the monobromide into tetrabromide, which reacting with the alkaline bromide present, formed bromoselenate. These reactions were all accompanied by evolution of heat. The excess of bromine was expelled on a water-bath, and on evaporation beautiful red crystals of bromoselenate separated. This method was found to be readily applicable in the preparation of inorganic bromoselenates.

In many double salts in which the ammonium group plays the part of alkaline metal, it is possible to replace the ammonia by an amine or aromatic base. In the case of platinum salts this takes place with ease, and subsequent experiments will show that tetrabromide of selenium unites with the salts of the fatty amines and aromatic bases to form well-defined analogous salts.

In the preparation of the organic derivatives recourse must be had to another means of preparation, since bromine in free condition acts on the organic bodies themselves.

## INORGANIC SALTS.

*Potassium Bromoselenate.*—This salt was prepared by the method above indicated, and was found to possess the same composition and properties as observed by Muthmann and Shäfer.

*Sodium and Lithium Salts.*—When the bromides of lithium and selenium or sodium and selenium are brought together, the mutual affinity is so small that no union occurs. On evaporating a solution of a mixture containing the respective salts, only alkaline bromide and selenious acid separated; neither exercise a sufficiently strong influence on the selenium to enable it to hold its bromine.

*Rubidium Bromoselenate.*—Pure rubidium bromide, tested spectroscopically and found to be free from cesium and potassium, was dissolved in water, selenium added, and bromine introduced. On evaporation at the low temperature of a water-bath, red crystals appeared, which examined under the microscope[1] showed the isometric combinations of cube and octahedron. In polarized light they proved to be isotropic.

On being subjected to analysis, the following data were obtained:

| Salt. Gram. | Se. Gram. | Se. Per cent. |
|---|---|---|
| 0.5015 | 0.0539 | 10.74 |
| 0.4999 | 0.0540 | 10.80 |

| Salt. Gram. | AgBr. Gram. | Br. Per cent |
|---|---|---|
| 0.5012 | 0.7760 | 65.88 |

The formula $Rb_2SeBr_6$ requires 10.82 per cent. Se and 65.72 per cent. Br.

The values used in calculation were: $Rb = 85.43$, $Se = 79.3$, $Br = 79.95$.

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[1] The microscopic examinations were made with the assistance of Professor A. P. Brown, and to him the author is indebted.

*Cesium Bromoselenate.*—Cesium carbonate was dissolved in pure hydrobromic acid, and the resulting bromide crystallized. When examined with the spectroscope this salt showed absence of potassium and rubidium salts. On treatment of the salt with selenium tetrabromide, there appeared on evaporation crystals similar, in appearance and properties, to the salts of rubidium and potassium.

Analysis gave:

| Salt. Gram. | Se. Gram. | Se. Per cent. |
|---|---|---|
| 0.5009 | 0.0479 | 9.56 |

| Salt. Gram. | AgBr. Gram. | Br. Per cent. |
|---|---|---|
| 0.5007 | 0.6860 | 58.29 |

Calculated for $Cs_2SeBr_6$, 9.73 per cent. Se, 58.16 per cent. Br. Cs = 132.89, Se = 79.3, Br = 79.95.

These salts are all soluble in water to a colorless solution. With the rise of atomic mass of the basic element, the solubility decreases, the rubidium salt being less soluble in water than the potassium salt, while the cesium salt is rather insoluble. This property may be expected, since the alums, and particularly the chloroplatinates of these positive elements show a corresponding decrease in solubility as the atomic mass rises.

Attempts were made to prepare the bromoselenates of barium and cadmium, but like sodium and lithium, these salts do not appear to exist.

The salts of thallium, in the lower state of oxidation, in many cases closely resemble the alkali salts, such as in the formation of double platinum salts, etc. No bromoselenate seems to exist. Selenium tetrabromide, prepared from this dioxide and hydrobromic acid, and hence obtaining no free bromine, tends rather to oxidize thallous salts to the thallic state than to form double salts.

*Ammonium bromoselenate* was prepared in a manner similar to that of the salts of rubidium and cesium. It is less soluble in water than the potassium salt. Analysis indicated the composition $(NH_4)_2SeBr_6$. The crystals exhibit the same isometric combination of cube and octahedron that the salts of potassium, rubidium, and cesium show. The salt was considered to be well adapted to accurate analysis, since ammonium bromide can be readily obtained pure both by sublimation and crystallization.

Analysis of the preceding salts was made by determining the bromine by precipitation with silver nitrate, in presence of sufficient free nitric acid to hold in solution the silver selenite which is simultaneously formed. The selenium was precipitated by hydroxylamine, and after washing with hot water, was brought upon an asbestos filter, dried at 100° and weighed.

## ORGANIC SALTS.

For the preparation of the organic derivatives two methods were found to be available. The first consisted in preparing selenium tetrabromide by direct bromination of finely divided selenium, with the vapors of bromine. Red crystals of tetrabromide were formed, which are very soluble in alcohol to a red brown color. When a concentrated alcoholic solution of the amine salt is treated with a strong alcoholic solution of tetrabromide, a precipitate is produced which consists of bromoselenate of the amine. This precipitate was dissolved in alcohol containing hydrobromic acid, and the resulting colorless solution allowed to crystallize spontaneously. Crystallization can be greatly hastened by placing the solution in a desiccator containing soda-lime, and exhausting the air.

A second method employed and a more satisfactory one, was to treat selenium dioxide with concentrated hydrobromic acid. Alcohol was added to the solution to take up the excess of water. By treating the amine salt dissolved in alcohol with this tetrabromide, salts were obtained identical with those obtained by the former method. The latter method is by far the cleaner method and the one to be preferred.

As a rule, the organic salts in appearance closely resemble the alkaline salts; they generally consist of fine red powder. Water decomposes them, hence they cannot be crystallized from it. Prolonged action of ether, more rapidly when warm, extracts selenium bromide.

*Methylamine Bromoselenate.* — Methylamine hydrochloride, containing ammonium salts, was treated[1] with caustic soda and distilled; the vapors were collected in dilute sulphuric acid. The

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[1] Fleck: This Journal, **18**, 670.

neutral solution of mixed sulphates of ammonium and methylamine was evaporated to dryness, and the residue extracted with absolute alcohol. Ammonium sulphate remained insoluble, methylamine sulphate passing into solution. After filtration, the alcohol was evaporated, the sulphate treated with sodium hydrate, when methylamine was liberated in pure condition. The gas was collected in hydrobromic acid. This latter solution, on evaporation, yielded pure methylamine hydrobromide.

When methylamine bromide was treated in alcoholic solution with selenium tetrabromide, a red precipitate formed, which on recrystallization from alcohol containing hydrobromic acid, gave a very finely crystalline body, which analyzed as follows:

| Salt. Grams. | Se. Gram. | Se. Per cent. |
|---|---|---|
| 1,0067 | 0.1266 | 12.57 |

| Salt. Gram. | AgBr. Grams. | Br. Per cent. |
|---|---|---|
| 0.9874 | 1.7829 | 76.83 |

The formula $(CH_3NH_3)_2SeBr_6$ requires Se 12.72 per cent. and Br 76.96 per cent. The values used in calculation were: $H = 1.008$, $C = 12.01$, $N = 14.04$, $Se = 79.3$, $Br = 79.95$.

*Ethylamine Bromoselenate.*—This salt was prepared from ethylamine bromide and selenium tetrabromide in a manner similar to the salt of methylamine. It forms flat hexagonal prisms, red in color. Analysis gave:

| Salt. Grams. | Se. Gram. | Se. Per cent. |
|---|---|---|
| 1.0008 | 0.1215 | 12.14 |

| Salt. Gram. | AgBr. Gram. | Br. Per cent. |
|---|---|---|
| 0.5619 | 0.9713 | 73.55 |

The formula $(C_2H_5NH_3)_2SeBr_6$ requires Se 12.17 per cent. and Br 73.66 per cent.

*Dimethylamine Bromoselenate.*—Dimethylamine was prepared by boiling nitroso-dimethylaniline with caustic soda; quinone oxime was formed, while at the same time dimethylamine was evolved as a gas, and collected in dilute acid. A good yield was obtained by this method. The salt obtained was again distilled with sodium hydroxide and the gas absorbed in dilute hydrobromic acid. After crystallization the bromide was dissolved in alcohol and treated with selenium tetrabromide. On allowing the alcoholic solution to evaporate, red crystals were obtained, similar in appearance to the salt of methylamine.

Analysis gave :

| Salt. Grams. | Se. Gram. | Se. Per cent. |
|---|---|---|
| 1.0233 | 0.1251 | 12.22 |

| Salt. Gram. | AgBr. Gram. | Br. Per cent. |
|---|---|---|
| 0.5227 | 0.9049 | 73.66 |

$[(CH_3)_2NH_2]_2SeBr_6$ is an isomeride of ethylamine bromoselenate and like it requires Se 12.16 per cent. and Br 73.66 per cent.

*Trimethylamine Bromoselenate.* — Trimethylamine was freed from contaminating ammonium salts, by treatment of the mixed sulphates with absolute alcohol, when the amine salt dissolves, leaving ammonium sulphate insoluble. Trimethylamine was liberated by treatment of the sulphate with caustic soda and absorbing the free amine in hydrobromic acid. The bromoselenate was prepared by adding a solution of selenium tetrabromide to trimethylamine bromide, dissolved in alcohol. The red precipitate formed was recrystallized from alcohol, when a fine red crystalline powder was obtained.

Analysis gave:

| Salt. Grams. | Se. Gram. | Se. Per cent. |
|---|---|---|
| 1.0010 | 0.1195 | 11.93 |

| Salt. Grams. | AgBr. Grams. | Br. Per cent. |
|---|---|---|
| 1.0501 | 1.7406 | 70.53 |

A determination of nitrogen by the Kjeldahl method gave 4.18 per cent. N. The formula $[(CH_3)_3NH]_2SeBr_6$ requires Se 11.68 per cent., Br 70.62 per cent., and N 4.13 per cent.

*Tetraethyl Ammonium Bromoselenate.*—The bromide was prepared by treating the base with hydrobromic acid. The bromoselenate was prepared in the same manner as previously described salts and crystallizes from alcoholic solution in minute flat hexagonal plates.

Analysis gave:

| Salt. Grams. | Se. Gram. | Se. Per cent. |
|---|---|---|
| 1.0021 | 0.0991 | 9.89 |

| Salt. Gram. | AgBr. Gram. | Br. Per cent. |
|---|---|---|
| 0.5366 | 0.7391 | 58.60 |

The formula $[(C_2H_5)_4N]_2SeBr_6$ requires Se 9.67 per cent. and Br 58.53 per cent.

It thus appears that all of the hydrogen atoms in ammonium bromoselenate can be replaced by a fatty amine. An entirely different behavior is shown by the aromatic amines. Aniline hydrobromide in hydrobromic acid solution precipitates selenium completely from a solution of selenium tetrabromide.

When an alcoholic or aqueous solution of selenium tetrabromide is treated with hydrobromide of aniline and filtered, the filtrate is found to be free from selenium, showing complete precipitation has taken place.

As might be expected from this behavior of aniline, diphenylamine in hydrobromic acid solution forms no derivative with selenium tetrabromide.

In the many reactions that were tried with phenylhydrazine, it appears that this substance seems to be almost as good a reagent for the precipitation of selenium as hydroxylamine.

*Pyridine Bromoselenate.*—Both pyridine and quinoline are strongly basic bodies of the aromatic series; the first forms a well-defined bromoselenate, while the second forms a compound which decomposes so readily with the separation of selenium that it is impossible to analyze it.

On treating pyridine hydrobromide in alcoholic solution with selenium tetrabromide, a crystalline precipitate is produced, which, recrystallized from alcohol, forms beautiful deep red scales. Under certain conditions it is possible to obtain the salt as prismatic crystals. This salt, like the salts of the fatty amines, dissolves in water to a colorless solution. Water, benzene, chloroform, ether, and carbon bisulphide dissolve in salt, but on evaporation of the solvent decomposition takes place, selenium separating. It has only been possible to obtain the salt from alcoholic solution.

A complete analysis was made; carbon and hydrogen were determined by combustion. Nitrogen was determined by the method of Dumas.

| Salt. Grams. | Se. Gram. | Se. Per cent. |
|---|---|---|
| 1.0011 | 0.1121 | 11.19 |

| Salt. Grams. | AgBr. Grams. | Br. Per cent. |
|---|---|---|
| 0.5007 | 0.7846 | 66.63 |
| 1.0057 | 1.5769 | 66.71 |

| Salt. Gram. | $H_2O$. Gram. | H. Per cent. |
|---|---|---|
| 0.4006 | 0.0645 | 1.79 |

| Salt. Gram. | $CO_2$. Gram. | C. Per cent. |
|---|---|---|
| 0.4006 | 0.2465 | 16.75 |

0.5151 gram of the salt gave 17 cc. of nitrogen, equivalent to 4.14 per cent.

The formula $(C_5H_5NH)_2SeBr_6$ requires H 1.67 per cent., N 3.90 per cent., Se 11.02 per cent., C 16.74 per cent., and Br 66.69 per cent.

Unless a slight excess of selenium tetrabromide is present in the solution undergoing crystallization, the salt dissociates to a slight degree. This fact and the tendency it showed to lose bromine, when dried over soda-lime, seem to be serious objections to its employment in an atomic mass determination.

*Piperidine Bromoselenate.*—Like pyridine, piperidine yields a strongly crystalline body with selenium tetrabromide. The salt was prepared in a manner similar to that of the pyridine salt. When crystallized from alcohol red tabular crystals appeared.

Analysis gave:

| Salt. Gram. | Se. Gram. | Se. Per cent. |
|---|---|---|
| 0.5002 | 0.0540 | 10.79 |

| Salt. Gram. | AgBr. Gram. | Br. Per cent. |
|---|---|---|
| 0.5305 | 0.8161 | 65.46 |

| Salt. Gram. | $CO_2$. Gram. | C. Per cent. |
|---|---|---|
| 0.4004 | 0.2422 | 16.49 |

| Salt. Gram. | $H_2O$. Gram. | H. Per cent. |
|---|---|---|
| 0.4004 | 0.1369 | 3.52 |

The formula $(C_5H_{11}NH)_2SeBr_6$ requires H 3.30 per cent., N

3.84 per cent., Se 10.84 per cent., C 16.46 per cent., and Br 65.59 per cent.

On standing over soda-lime, this salt, like the pyridine compound, slowly loses bromine.

When the mother-liquor from which the red soluble crystals were obtained was allowed to slowly evaporate, a black salt appeared, from which, when treated with water, large quantities of selenium immediately separated. Analysis of various samples of this black compound gave determinations of selenium from 11.79–14.39 per cent. Bromine estimations indicated a variation in content from 67.42 per cent. to 70.71 per cent. From the irregularities in composition of different samples and the variations in color from red to black, it would appear that piperidine bromoselenate, when crystallized from solutions containing an excess of selenium tetrabromide, tends to enclose the latter and carry it down with it.

## THIRD SECTION.

### SELENIUM MONOXIDE.

Different chemists at various times have either affirmed or denied the existence of the monoxide of selenium. Berzelius ascribes the odor of rotten horseradish, noticed when selenium burns in air, to the existence of this oxide. Chabrie,[1] in his work on the organic derivatives of selenium, claims to have prepared the monoxide by heating selenium to 180° in air. So firmly convinced was he that the monoxide exists that he used this method as a means of estimating selenium. A. W. Pierce[2] has made an investigation of Chabrie's work, and concludes that it is probably not formed by the method of Chabrie, and thinks the odor produced when selenium is burned in air is due to the presence of moisture, which, under the circumstances, would produce hydrogen selenide.

While subliming the large quantities of pure dioxide used in the preceding investigation, at no time was there noticed an odor like that produced when selenium burns in air or when a selenide is roasted. On the contrary, the vapor of selenium

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[1] *Ann. chim. phys.* [6], 20, 273.

[2] *Ztschr. anorg. Chem.*, 13, 121.

dioxide which at times escaped into the air, gave an odor much resembling that of sulphur trioxide.

An experiment was made to determine whether selenium would reduce the dioxide when heated in an open vessel at the atmospheric pressure. No combination was found to take place.

A second experiment was made, in which equivalent parts by weight of selenium and dioxide were placed in a stout glass tube of hard glass, about forty inches long by one-half inch internal diameter. The tube was sealed and heated in a large flame, until the selenium melted. The dioxide under the pressure generated by its own volatilization, melted to a thick liquid. The temperature was raised to the boiling-point of selenium. Should selenium be able to reduce the dioxide, it should do so in a solution of the combined gases. Such, however, is not the case; on cooling, the mass resolves itself into separate layers of selenium and dioxide. When the tube was opened, no pressure was observed (such as would have been the case had a gas been formed), nor could any odor be detected. On treating the mass with water, selenious acid was formed, which dissolved, leaving selenium insoluble.

Selenium and tellurium have many derivatives from which well-established analogies can be drawn. Where a derivative of one element exists, a corresponding derivative of the other is usually found. That tellurium forms a monoxide, there can be little doubt, hence it has seemed probable that a monoxide of selenium should exist. However, in considering their halides, we find that while tellurium forms the compounds $TeX_2$ and $TeX_4$, directly analogous to the oxides TeO and $TeO_2$, selenium forms only those halides of the types $Se_2X_2$ and $SeX_4$, the latter corresponding to the well-known $SeO_2$. From the analogy thus established between the oxygen and halogen derivatives, one would rather expect an oxide $Se_2O$ than SeO. It was therefore thought that the lower oxide might be prepared by treatment of the monobromide with dry silver oxide. $Se_2Br_2$ was prepared by rubbing the tetrabromide with selenium. No action could be brought to take place between silver oxide and a solution of the bromide in carbon disulphide. When the liquid bromide is treated at the ordinary temperature with silver oxide, a violent reaction takes place. Much heat is evolved, the reaction being explosive in character. The resulting mass on treatment with water gives a solution containing only selenious acid.

If the monoxide is formed it is likely that the heat of the reaction would decompose it. The experiment was subsequently modified by chilling the bromide to —7°. At this temperature, silver oxide swims unattacked on the surface of the liquid monobromide. No reaction takes place until the whole attains a temperature of +20°, when the same violent reaction takes place that was before noted. On conducting the experiment in a closed tube, it is noticed that on opening the tube, no pressure exists, hence it is unlikely that a gas has been formed. Should a lower oxide be formed at all in this reaction, the experiments seem to indicate that it immediately dissociates into selenium and the dioxide.

As Pierce has pointed out, it seems very likely that the odor noticed when selenium is roasted in air, is due to the presence of hydrogen selenide, and that efforts to obtain other oxides than the dioxide, thus far have been unsuccessful.

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# OSMOTIC PRESSURE.

BY C. L. SPEYERS.

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CONSIDER the following arrangement: The lower vessel contains pure solvent; the tube contains a solution of some non-volatile body in that solvent. The tube is open at the top but closed at the bottom by a diaphragm permeable to the solvent only. At equilibrium, the arrangement is to be so