this reduction. Sterba attributed its spontaneous combustion to the formation of finely divided metallic cerium, which assumption the above results show is erroneous, however, as does also the work of Newberry and Pring previously mentioned.

## Summary.

It has been shown that the decomposition of cerous oxalate, and resulting carbonate, in a hydrogen or nitrogen atmosphere, yields a bluish black mixture of $CeO_2$, $Ce_4O_7$ and carbon.

This residue when prepared in hydrogen will take fire if drawn directly from that atmosphere into the air, due to oxidation of adsorbed hydrogen; it is capable of adsorbing that gas to the extent of from 51 to 58.5 times its own volume under the conditions worked with.

Qualitatively the residue shows the same composition whether prepared in hydrogen or nitrogen.

Several analyses of residues prepared in hydrogen are given, the mean of which indicate a composition as follows: $CeO_2$ 53.96, $Ce_4O_7$ 39.49, C 2.64, absorbed air 3.43%, respectively.

$CeO_2$ and $Ce_4O_7$ have been shown to possess in marked degree the power of adsorbing gases.

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# A STUDY OF TANTALUM CHLORIDE WITH REFERENCE TO ITS USE IN THE DETERMINATION OF THE ATOMIC WEIGHT OF TANTALUM.

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A consideration of the ratios that have been studied for the determination of the atomic weight of tantalum shows that they have almost universally involved the use of either tantalum chloride or tantalum oxide. In 1866 Magrignac[1] established the formula of tantalum oxide and studied a number of ratios only one of which did not involve either the chloride or the oxide. Since that time four ratios have been studied. Hinrichson and Sahlbom[2] in 1906 determined the ratio $2Ta : Ta_2O_5$ by direct ignition of the metal to the oxide. In 1910 Balke[3] converted the chloride into the oxide by hydrolysis and subsequent ignition with nitric acid, obtaining the ratio $2TaCl_5 : Ta_2O_5$. The same process was used by Chapin and Smith[4] in 1911 in the study of the ratio $2TaBr_5 : Ta_2O_5$. In 1915 Sears and Balke[5] published an investigation of the ratios $2TaCl_5 : Ta_2O_5$ and $TaCl_5 : 5Ag$ in which it was found that tantalum oxide obtained from the

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[1] Abegg's "Handb. der Anorg. Chem.," [3] **3**, 839.

[2] *Ber.*, **39**, 2600 (1906).

[3] THIS JOURNAL, **32**, 1122 (1910).

[4] *Ibid.*, **33**, 1497 (1911).

[5] *Ibid.*, **37**, 833 (1915).

chloride by hydrolysis and subsequent ignition with nitric acid not only occludes the nitric acid but is itself lost during ignition. It was also found that tantalum chloride when prepared by passing sulphur monochloride and chlorine over heated tantalum oxide and transferred in an atmosphere dried with concentrated sulfuric acid was not of constant composition.

In view of the fact that tantalum chloride has played such an important part in establishing the constant a further study of this compound was undertaken with the idea of ascertaining its value as a basis for the determination of the atomic weight of tantalum.[1]

## Preparation of Materials.

The tantalum chloride used in this investigation was prepared by passing chlorine and sulfur monochloride vapor over heated tantalum oxide, obtained from potassium tantalum double fluoride, which had been carefully purified by recrystallization. Special care was taken in the preparation and purification of all reagents. The methods employed for the preparation of all materials were essentially the same as those described in the earlier investigation.[2] All weights were made on one of Ruprecht's best balances.

## Experimental.

Pure tantalum chloride contained in a sealed bulb was placed in a closed glass tube connected with a manometer capable of measuring pressures as high as one atmosphere. The whole apparatus was then carefully dried by repeated evacuation and replacing with air dried with concentrated sulfuric acid and phosphorus pentoxide. During the process the whole apparatus was warmed from time to time. Finally the apparatus was evacuated and sealed off. The bulb containing the tantalum chloride was then broken and the temperature and pressure noted. Two experiments were carried out. In the first the evacuation was carried down to 23 mm. After standing at room temperature for a week the pressure showed an increase of only 4 mm. The tantalum chloride was then heated to the sublimation point. After cooling the pressure was again read. A very marked increase was shown by the manometer. The sublimation was repeated several times during which the pressure gradually increased to a nearly constant value of 56 mm. The mercury in the manometer tube showed that it had been acted on to a slight extent by the evolved gas. In a second experiment the evacuation was carried down to only 194 mm. On standing a gradual increase in pressure was noticed, which became more marked after vaporization. After several vaporizations, however, the pressure became practically constant. The whole apparatus

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[1] The author wishes to take this opportunity of expressing sincere thanks to Dr. C. W. Balke for many helpful suggestions during the early part of this investigation.

[2] This Journal, 37, 833 (1915).

was allowed to stand for about a month after which the tantalum chloride was again vaporized. No change in pressure was obtained.

The result of these two experiments seemed to indicate therefore that the tantalum chloride either dissociated giving off free chlorine or was decomposed by traces of moisture which may not have been removed in the process of drying the apparatus.

A second series of experiments was then carried out in which dry air or nitrogen was passed over tantalum chloride and the resulting gas mixture tested for possible dissociation or decomposition products. A bulb of the tantalum chloride was placed in a glass tube both ends of which were sealed to tubes containing resublimed phosphorus pentoxide. A current of dry air was then passed through the apparatus for three days during which it was warmed from time to time so that all traces of moisture would be removed. The bulb containing the tantalum chloride was then broken and a slow stream of dry air was passed through the apparatus and allowed to bubble through a silver nitrate solution. A very decided opalescence was obtained even after the gas had been running for two days. The apparatus was then surrounded with a freezing mixture but this seemed to make very little difference in the amount of turbidity obtained in the silver nitrate. The air was then replaced by dry nitrogen but with no appreciable change in the amount of turbidity.

A second apparatus was prepared in the same way except that the exit tube consisted of about six feet of capillary tubing instead of the tube containing phosphorus pentoxide. After careful drying, the bulb containing the tantalum chloride was broken and pure dry nitrogen was passed through the apparatus and allowed to bubble through pure water contained in a weighed platinum crucible. After the gas had been passed for nine hours a part of the water was removed and tested with silver nitrate. The presence of a considerable amount of chloride was shown. The remainder of the water in the crucible, about 25 cc., was evaporated to dryness and the crucible again weighed. No increase in weight was found. It was therefore evident that the presence of chloride could not have been due to tantalum chloride vapor but must have been in the form of hydrochloric acid. Though special precautions had been taken for excluding all moisture yet it seemed that hydrolysis was taking place.

With this idea in mind a third experiment of like nature was carried out in such a way as to exclude all possibility of moisture in the apparatus. Tantalum chloride was prepared as before and distilled directly into a tube fitted with two special joints of the type used by Briscoe and Little[1] which enabled one to make a sealed connection without exposing the contents of the tube. To one of the joints was sealed a tube containing phosphorus pentoxide which had been freshly sublimed into it and to the other

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[1] *J. Chem. Soc.*, 105, 1310 (1914).

was sealed about six feet of capillary tubing. Special care was taken to dry thoroughly the connections and the capillary tube before admitting the gas to the tube containing the tantalum chloride.

Nitrogen passed over hot copper and copper oxide to remove the last traces of oxygen and hydrogen was dried by passing through two towers about two feet high containing glass beads over which concentrated sulfuric acid was allowed to drip from time to time, then through the tube containing freshly sublimed phosphorus pentoxide. From this the gas was conducted over the tantalum chloride with the following results: The chlorine atmosphere was completely replaced by nitrogen in about an hour as shown by the potassium iodide-starch test. At room temperature no decomposition or dissociation could be detected with silver nitrate even after allowing the nitrogen to remain in contact with the tantalum chloride overnight and subsequently testing with silver nitrate.

The tantalum chloride was then melted and the gas tested for chlorine but with negative results. A positive test for chloride, however, seemed to indicate that decomposition had taken place but this was later shown to be due to tantalum chloride vapor carried over in the current of nitrogen. The nitrogen was then replaced with dry air. No decomposition or dissociation was shown either at room temperature or that of the melted tantalum chloride.

The conclusion, therefore, is that tantalum chloride is of constant composition and does not occlude chlorine but that it is hydrolyzed in an atmosphere which has not been dried with the very best phosphorus pentoxide.

The question of analysis was next taken up with the idea of determining, if possible, the ratio $TaCl_5 : 5Ag$. Since the chloride can be determined only in the presence of considerable amounts of hydrofluoric acid[1] analysis of the tantalum chloride necessitated its transfer from a sealed glass bulb in which it was prepared to a platinum reaction flask. An attempt was first made to transfer the chloride to a platinum weighing bottle provided with a ground-in stopper. For this purpose the apparatus shown in Fig. 1 was used. The bulb containing the tantalum chloride was placed at A and a weighed platinum bottle at B, the stopper of which was hung at C. The sliding joints at D, D′ and D″ were made air-tight by means of closely fitting rubber tubing.

In order to make the transfer the bulb was broken by means of an electrically heated platinum wire, G. The platinum bottle was then slipped over the neck of the bulb, which served as a funnel, and the apparatus tipped so as to allow the tantalum chloride to run into the weighing bottle. The bottle was then moved back far enough to allow the stopper to be shoved up and inserted by means of the rod E.

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[1] THIS JOURNAL, 37, 833 (1915).

Considerable difficulty was encountered in drying the apparatus sufficiently. It was found necessary to heat the whole apparatus at 120–130° for several hours while dry air was being passed through in order to obtain an atmosphere dry enough to make the transfer without hydrolysis. In order to detect possible hydrolysis after the transfer had been made, the two-way stopcock F was turned and the air within the apparatus was run into a solution of silver nitrate.

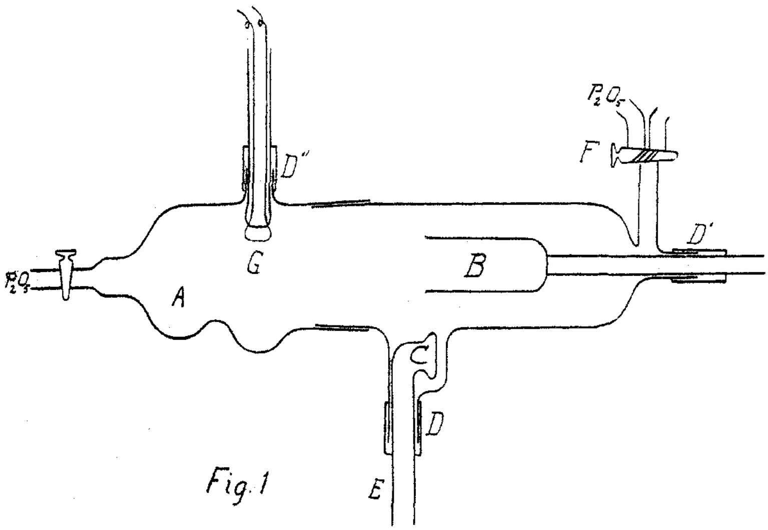

Fig. 1

Although the tantalum chloride could be transferred to the weighing bottle without difficulty by means of this apparatus it was soon found that it could not be weighed accurately because of hydrolysis and consequent loss of chlorine, evidently due to diffusion through the ground joint of the stopper. The amount of the loss is illustrated by the weights 3.93256, 3.93217, 3.93190, which were obtained for the same sample of tantalum chloride on three consecutive days. A second sample treated in the same way gave the following weights: 3.64490, 3.64446, 3.64435. It is seen, therefore, that an actual loss of more than 0.4 mg. is occasioned by standing one day in a vessel closed with a ground-in stopper. Since a loss of 0.1 mg. from a 4 g. sample of tantalum chloride makes an error of nearly 0.03 of a unit in the atomic weight it is evident that a high degree of accuracy cannot be obtained by this process.

In order to prevent this loss the platinum bottle was placed in one of glass fitted with a carefully ground-in stopper. Diffusion, however, could not be prevented until the glass-stoppered bottle was provided with a mercury seal and the mercury protected from evaporation by a second stopper. With this arrangement a constant weight could be obtained but in every case when the stoppers were removed from the glass bottle the odor of hydrochloric acid was detected, showing that hydrolysis had taken place.

An attempt was then made to obtain an accurate weight of tantalum chloride in a sealed vessel. Broken glass could not be filtered off from the hydrolyzed tantalum chloride because of the insoluble tantalic acid formed. Of the possible methods of procedure, therefore, the only one that seemed at all feasible was to transfer the tantalum chloride to a weighed glass vessel which might subsequently be sealed off. The value of this procedure would depend not only on the volatility of the glass but also on the ability to make the seal without melting tantalum chloride into the glass.

The effect of volatility of the glass was determined by noting the change in weight of a glass rod caused by melting a portion of it. A small, irregular though very definite loss was obtained in every case.

A study of the transfer of tantalum chloride into the bulb to be sealed off was then taken up. For this purpose the tantalum chloride was distilled into a horizontal glass tube which was connected by means of a ground joint to a weighed glass bulb. The neck of the bulb was protected from the tantalum chloride particles by means of a funnel tube extending well into it. The transfer was made by pulling the chloride into the mouth of the funnel with a glass rod bent at one end. The bulb was then carefully sealed off just below the funnel tube but in every case the seal showed that small amounts of the chloride had been melted into the glass. It is evident, therefore, that any analysis of tantalum chloride based on its weight obtained in a sealed tube cannot claim for itself a very high degree of accuracy.

## Summary.

The results of this investigation may be summarized as follows:

1. Tantalum pentachloride exists as a stable compound in an atmosphere of dry nitrogen or air.
2. It does not occlude chlorine.
3. It is hydrolyzed in an atmosphere not dried with the very best phosphorus pentoxide.
4. A high degree of accuracy cannot be obtained in the analysis of tantalum chloride when weighed in a vessel containing a ground joint or when sealed in a weighed tube owing to diffusion of moisture through the joint and volatility of the glass, respectively.

It seems, therefore, from the results of this investigation that tantalum chloride is unsuitable for use in work where a high degree of accuracy in its analysis is desired. A further study of tantalum and its compounds is now in progress with the hope of obtaining a satisfactory ratio.

URBANA, ILL.