of general practical interest is that the active substance concentrates in the front. This is a most favorable circumstance, since in practice it is much easier to maintain the front boundary perfectly sharp than the rear. This concentration in front shows that the mesothorium I and radium ions have greater mobilities than the barium ion, so that the increase in ionic mobility with atomic weight is maintained throughout the whole alkaline earth group.

Summary

The application of the ionic-migration method to the separation of radium and mesothorium I from barium has been investigated. It has been shown that the mobility of these radioactive ions exceeds that of barium to a sufficient degree to permit, by this method, a practicable separation of radium, mesothorium I, or mixtures of radium and mesothorium I from barium.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY, HARVARD UNIVERSITY]

A REVISION OF THE ATOMIC WEIGHT OF TITANIUM. THE ANALYSIS OF TITANIUM TETRACHLORIDE. II

BY GREGORY PAUL BAXTER AND ALBERT QUIGG BUTLER

RECEIVED OCTOBER 28, 1926 PUBLISHED DECEMBER 16, 1926

In a recent preliminary paper by Baxter and Fertig[1] the purification and analysis of a specimen of titanium tetrachloride are described. The atomic weight of titanium thus found, 47.9, is considerably lower than that obtained by Thorpe,[2] 48.1, which has been universally accepted for some time. We have continued the analysis of the fractions of titanium tetrachloride prepared by Baxter and Fertig and have obtained essentially the same result.

The purification of the titanium tetrachloride by fractional distillation in exhausted, sealed apparatus with the use of Hempel fractionating columns is described in detail in the earlier paper by Baxter and Fertig. In Fig. 1, which gives an outline of the fractionation, the large lettered circles represent the separate fractionations, while the fractions removed in each distillation are shown by small circles. All the fractions which have been analyzed are numbered in the order of decreasing volatility; that is, in Fractionation O the most volatile fraction is 2 and the next to the least volatile 24. The atomic weight of titanium found from each fraction is also shown in the diagram. Earlier spectroscopic examination had failed to disclose impurity in the distilled material, and the uniformity in atomic weight found from fractions removed at different stages in the

---

[1] Baxter and Fertig, THIS JOURNAL, **45**, 1228 (1923).

[2] Thorpe, *Ber.*, **16**, 3014 (1883); *J. Chem. Soc.*, **47**, 108 (1885).

distillation is further evidence that the fractional distillation was adequate purification.

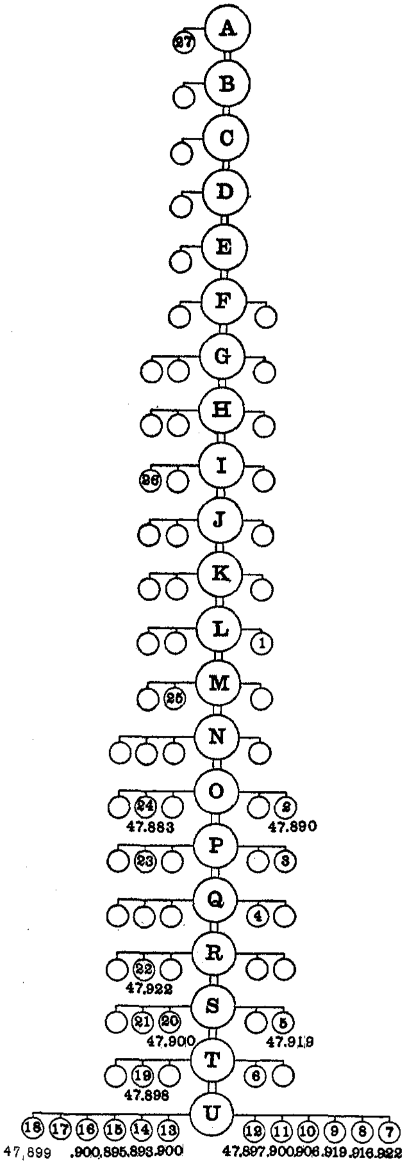

Fig. 1.

The present paper deals chiefly with refinements in the method of analysis as carried out by Baxter and Fertig. In outline this method consisted first in breaking the weighed bulb containing titanium tetrachloride under nitric acid and collecting the glass for weighing. After the solution had been diluted the chloride was precipitated with a solution of a weighed nearly equivalent amount of pure silver. The point of equivalence was then found with the assistance of a nephelometer.

Although Hönigschmid[3] has found that solution even in 3 N nitric acid involves no loss of chlorine from chlorides at room temperature, owing to the danger of evaporation during filtration of the glass, we made careful tests to prove that no such loss actually took place. A solution of titanium tetrachloride in normal nitric acid was filtered by suction through a platinum sponge crucible into a receiver under a bell jar, while the air removed from the bell jar was drawn through a U-tube containing ammonia. The ammonia solution after evaporation was found by nephelometric comparison to contain 0.04 mg. of chlorine. In a second similar experiment in which the same solution was filtered into a large bottle the amount of chlorine found was 0.005 mg. A still more rigid test was then made by drawing air at a slow rate first through the same solution of the tetrachloride in N nitric acid and then through dilute ammonium hydroxide. In three experiments of two, three, and two and one-half hours'

---

[3] Hönigschmid, *Z. Elektrochem.*, **26**, 403 (1920); *Ber.*, **54B**, 1873 (1921).

duration the amounts of chlorine found were 0.003, 0.002 and 0.004 mg., respectively. Since in all the experiments except the first the chlorine evaporated is insignificant in amount, nitric acid of normal concentration is evidently a safe solvent for the chloride during filtration. Actually, the solution was in nearly every case considerably less acid than this when filtered.

In the preliminary work by Baxter and Fertig the fragments of the glass bulbs were collected on a filter paper, which was subsequently burned. These authors were unable to obtain certain evidence that any titanium was retained under these conditions. In the present work, after the glass had been washed by decantation with pure water it was collected on a weighed platinum sponge crucible and the crucible was dried at 250° for 15 hours before being weighed. In order to remove adhering titanium hydroxide the crucible and contents were next washed with nitric acid by repeatedly pouring 500 ml. of hot 6 *N* acid through the crucible until the loss in weight became negligible. Usually this did not require more than two treatments. The fact that the weight of the glass quickly became constant is evidence that the effect of the nitric acid on the glass itself was not serious. The nitric acid washings were discarded.

Thorpe[2] decomposed the titanium halides with relatively small quantities of water and states that the solutions obtained were clear. Our experience was that at concentrations high enough to give this result halogen acid evaporated from the solution. This may account for the higher atomic weight found by him. Therefore, as in the experiments of Baxter and Fertig, the titanium tetrachloride was dissolved in a considerable volume of nitric acid. In the first five experiments the acid was 2 *N*, in the next four it was 1 *N* and in the last eight it was 1.5 *N*. In all cases the initial turbidity of titanium hydroxide completely disappeared in the course of from 8 to 48 hours according to the concentration of the acid. At the expiration of this period the solution was diluted to an acid concentration of from 0.16 *N* to 1 *N* before the glass was filtered out. Except in Analysis 6, in which the acid was 0.16 *N* after dilution, the solution remained perfectly clear.

The complete outline of the analytical method is as follows. After being cleaned with chromic acid mixture the density of the bulb containing the tetrachloride was found by weighing the bulb submerged in water of known temperature and then by substitution in air of known density.[4]

The weighed bulb was then broken under 250 ml. nitric acid in a heavy-walled, glass-stoppered flask, and the solution was allowed to stand until clear. After dilution to from twice to thrice the volume (in Analyses 4, 5 and 6 to six times) the solution was filtered through a weighed platinum

---

[4] Found by weighing a standardized sealed globe in air [Baxter, THIS JOURNAL, **43,** 1317 (1921)].

sponge Gooch crucible and the glass was collected and weighed as previously described.

The weight of the titanium tetrachloride was obtained by subtracting from the weight of the bulb corrected to vacuum the weight of the glass also corrected to vacuum. Very nearly the exact weight of pure silver necessary to combine with the tetrachloride was dissolved in nitric acid with especial precautions to avoid loss by spattering and after dilution until approximately 0.1 *N* the solution was slowly added to the chloride solution which also had been diluted to about half the above-mentioned concentration with either water or nitric acid. The final acidity of the chloride solution varied considerably. In Analysis 17 it was 1 *N*, in Analyses 1, 15 and 16, 0.5 *N*; in Analyses 2, 3, 4, 5, 10, 11, 12, 13, 14, 0.2–0.3 *N*, and in Analyses 6 to 9 it was 0.1 *N*. Thorough shaking and standing for several days followed. With the aid of a nephelometer the chloride and silver in the solution were adjusted until exactly equivalent. As is usually the case, several weeks elapsed before the end-point became constant, owing apparently to slow extraction of occluded material from the precipitate.

Vacuum corrections were applied as follows.

	Density	Vacuum correction per g.
Weights	8.3	
Silver	10.49	−0.000031
Glass	2.5	+ .000335
Air	0.001293 (0° and 760 mm.)	

Weights were standardized by the substitution method of Richards.[5]

TABLE I

ATOMIC WEIGHT OF TITANIUM

$TiCl_4$:4 Ag

Ag = 107.880 Cl = 35.458

Analysis	Fraction of $TiCl_4$	Wt. of $TiCl_4$ in a vacuum, g.	Wt. of Ag in a vacuum, g.	Wt. of Ag added or subtracted in solution, g.	Corrected weight of Ag in a vacuum, g.	Ratio, $TiCl_4$: 4 Ag	At. wt. of Ti
				PRELIMINARY SERIES			
1	2	4.65029	10.57911	−0.00211	10.57700	0.439660	47.890
2	24	4.84172	11.01561	− .00280	11.01281	.439644	47.883
3	22	4.56353	10.38134	− .00340	10.37794	.439734	47.922
4	20	5.96411	13.56543	− .00083	13.56460	.439682	47.900
5	19	5.52182	12.55838	+ .00040	12.55878	.439678	47.898
6	5	4.36899	9.93650	− .00080	9.93570	.439726	47.919
7	7	4.81128	10.94305	− .00170	10.94135	.439734	47.922
8	8	4.22304	9.60656	− .00263	9.60393	.439720	47.916
9	9	4.94516	11.24739	− .00144	11.24595	.439728	47.919
					Av.	.439701	47.908

---

[5] Richards, THIS JOURNAL, **22**, 144 (1900).

TABLE I (*Concluded*)

Analysis	Fraction of $TiCl_4$	Wt. of $TiCl_4$ in a vacuum, g.	Wt. of Ag in a vacuum, g.	Wt. of Ag added or subtracted in solution, g.	Corrected weight of Ag in a vacuum, g.	Ratio, $TiCl_4$: 4 Ag	At. wt. of Ti
				FINAL SERIES			
10	10	4.29334	9.76432	0.00000	9.76432	0.439697	47.906
11	12	5.25291	11.94758	− .00035	11.94723	.439676	47.897
12	14	5.64352	12.83564	+ .00025	12.83589	.439667	47.893
13	16	5.02562	11.43021	− .00010	11.43011	.439683	47.900
14	18	3.66098	8.32645	.00000	8.32645	.439680	47.899
15	11	4.22599	9.61128	+ .00020	9.61148	.439682	47.900
16	13	4.86075	11.05526	− .00010	11.05516	.439682	47.900
17	15	4.86836	11.07244	+ .00030	11.07274	.439671	47.895
					Av.	.439680	47.900
				Av. of all determinations		.439691	47.903

Conditions of precipitation seemed to be of little influence except in Analyses 6 to 9, where the acidity of the titanium solution was only 0.1 *N* during precipitation. In these analyses the supernatant solution contained colloidal titanium hydroxide, so that the end-point of the titration was difficult to determine. The results of these analyses are perceptibly higher than all but one of the others. On the whole the last eight analyses were freer from uncertainties than the first nine and therefore are grouped by themselves, but the average of these eight shows only slight deviation from that of all.

After the end-points had been reached, in five determinations the silver chloride was collected with the precautions usual in very exact work and weighed. The atomic weight of titanium calculated from the weight of silver chloride varied from 47.799 to 47.896. These lower results were found to be due to titanium occluded presumably as hydroxide by the silver chloride, for the silver chloride precipitates were found by spectrographic examination to contain considerable and variable amounts of the above impurity.

The final outcome of our analyses of titanium tetrachloride is, therefore, that the atomic weight of titanium is 47.90 (Cl = 35.458), a value which is in accordance with the earlier result of Baxter and Fertig. If Cl = 35.457, the atomic weight of titanium is not affected in the second decimal place.

CAMBRIDGE, MASSACHUSETTS