metals have undoubtedly been affected adversely by the presence of the aluminum. That this is so is indicated by the fact that a greater activity was found for pure cerium, as shown in Fig. 2, than for a 50–50 aluminum-cerium alloy, the curve for which is shown in Fig. 3. It is obvious from the curve shown in Fig. 3 for aluminum-tungsten that the increased emission due to these alloys cannot be ascribed to the presence of the aluminum.

The authors take pleasure in expressing their thanks to Mr. Lawrence Ferguson of this Laboratory for his assistance in taking these measurements.

## Summary

1. Data are presented in this paper which indicate that rare-earth metals of the cerium and yttrium groups are without exception much more active thermionically than the commonly occurring metals. The electron emission from some of these rare earth metals was found to be about a million times as great as that from clean tungsten at the same temperature.

2. Two methods for the determination of the thermionic activities of materials obtainable in powdered form have been described.

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[Contribution from the Chemistry Department of Columbia University, No. 522]

# THE SEPARATION OF RADIUM AND OF MESOTHORIUM I FROM BARIUM BY THE IONIC MIGRATION METHOD

By James Kendall, Eric R. Jette and William West

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The separation and concentration of radioactive substances is an important problem which appears amenable to treatment by the ionic-migration method, and we have therefore performed experiments to ascertain to what extent the method is applicable to the separation of radium and its isotope mesothorium I from the barium by which they are always accompanied. The standard commercial procedure involves a long series of fractionations of the barium residues, and it has already been shown in the case of typical rare-earth mixtures that a much more rapid and convenient separation may be effected by taking advantage of differences in ionic mobility rather than differences in solubility.

As the details of technique have been fully described in previous reports,[1] it will suffice here to state that the method depends on the fact that if radium and barium ions possess appreciably different mobilities, the migration, in the process of electrolysis, of a section containing these ions will be accompanied by a gradual concentration of the faster ion in front and of the slower behind. The boundaries of the moving section may be maintained sharp by causing it to be preceded by a still faster ion and

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[1] Kendall and Crittenden, *Proc. Nat. Acad. Sci.*, **9**, 75 (1923). Kendall and Clark, *ibid.*, **11**, 393 (1925).

followed by a still slower ion of suitably adjusted concentration and, to facilitate handling, the whole electrolyte, except that near the electrodes, is incorporated in an agar gel. Any accumulation of radioactive material at one or other end of the section will be shown by an increase in the ratio of the activity to the amount of salt present in the region in question. It is true that, under certain circumstances, the conclusions to be drawn from such a change in activity might not be quite unequivocally indicated, for a radioactive substance contains, in general, a mixture of active disintegration products of possibly different mobilities and, moreover, these products are being continually formed in the course of an experiment; but if, as in the case studied, the average lives of the products are short in comparison with that of the initial element, any considerable change in the observed activity ratio would indicate without ambiguity a change in the concentration of the parent substance.

**Material.**—A commercial sample of mesothorium bromide (kindly furnished by Dr. H. S. Miner of the Welsbach Company) containing 21 mg. of mesothorium to 1000 g. of barium bromide was employed, and like all such samples it contained an appreciable quantity of radium. A small amount of barium bromide containing radium was also available, by courtesy of the United States Radium Corporation, but since it has been conclusively shown that radium and mesothorium I are isotopic,[2] and since all experimental evidence hitherto obtained concerning the mobilities of isotopic ions is to the effect that they are, for practical purposes, identical,[3] it was possible to use mesothorium I in all experiments instead of the less plentiful radium, with the assurance that any results obtained would apply equally well to both elements. Even if, as a result of the migration, there might possibly be a change in the ratio of mesothorium to radium in various parts of the sample, the order of magnitude of such a separation would certainly be entirely too small to be detected by the methods used in the present investigation.[4]

**Experimental.**—As the result of several preliminary experiments, the following conditions were finally chosen as most advantageous. The radioactive section, 5 cm. long, was made 0.5 *N* with respect to barium, and contained 2.5% of agar. It was preceded by a column of 0.62 *N* potassium chloride, and followed by 0.4 *N* cupric chloride, also in 2.5% agar gels. The rear boundary was readily followed as the cupric ion migrated along the tube. The migration tube, 3 meters long, fitted into large flasks containing the electrode liquids, 0.4 *N* copper chloride with a suspension of copper hydroxide at the anode, and 0.6 *N* hydrochloric acid at the cathode.

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[2] Strong, This Journal, **43**, 444 (1921).

[3] Kendall and White, *Proc. Nat. Acad. Sci.*, **10**, 458 (1924). Pilley, *Phil. Mag.*, **49**, 889 (1925).

[4] Jette, article in press.

Under a potential difference of 400 volts the radioactive section was caused to move twice through the tube, a distance of 500 cm., in eight days, with practically no change in length.

On completion of a migration, the radioactive section was divided in the usual manner, and the segments, after being dried and freed from carbonaceous material, were tested for their activity by the $\alpha$-ray electroscope. The procedure was to observe by means of a stop-watch the time taken for the leaf to move between two given scale divisions; activities were then expressed as scale divisions traversed by the leaf per minute, allowance being made, when necessary, for the natural leak of the instrument.

**Results.**—Preliminary experiments showed that a considerable concentration of radioactive substance towards the front of the segment was readily produced. This is exemplified in Table I, which contains illustrative data for such an experiment.

TABLE I

PRELIMINARY RESULTS

| Segment no. | Wt. of segment, g. | Activity | Activity per unit wt. |
|---|---|---|---|
| 20 (front) | 0.042 | 19.7 | 468 |
| 7 (rear) | .022 | 1.5 | 68 |

In a final run, the ratio of the activity to weight of barium (plus radioactive material) in the segments was more carefully determined. The segments, after being dried and freed from carbon by evaporation with nitric acid and conversion of the nitrate to chloride, were dissolved in water, and the barium was precipitated as sulfate, carrying with it the mesothorium I, the radium and some short-lived disintegration products with sparingly soluble sulfates. In the measurement of the activities of these precipitates, values were obtained for all the segments in turn, and the series was repeated. The two series of values were concordant, hence the variations found cannot be attributed to the decay of a product of short average life. The ratio of the activity to the weight of sulfate precipitate for the different segments, and also for the unmigrated material, are given in Table II.

TABLE II

FINAL RESULTS

| Segment no. | Wt. of ppt., g. | Activity | Activity/wt. of ppt. |
|---|---|---|---|
| 6 (front) | 0.0159 | 16.4 | 1031 |
| 5 | .0380 | 20.8 | 547 |
| 4 | .0340 | 4.8 | 223 |
| 3 | .0421 | 5.4 | 128 |
| 2 | .0266 | 3.0 | 113 |
| 1 (rear) | .0289 | 2.8 | 99 |
| Unmigrated sample | 0.15 | 50 | 333 |

It is evident that the method is capable of causing a very considerable and rapid concentration of radioactive material in barium residue. A point 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.

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[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

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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

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

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