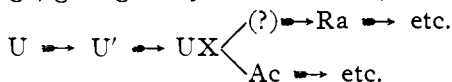


rays and the inactive product which finally produces radium; the second, much slower change, giving  $\alpha$ -rays and actinium, thus:



Oct. 12, 1907.

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO].  
**THE SPECIFIC RADIOACTIVITY OF THORIUM AND THE VARIATION  
 OF THE ACTIVITY WITH CHEMICAL TREATMENT  
 AND WITH TIME.**

BY HERBERT N. MCCOY AND W. H. ROSS.

Received October 14, 1907.

In our first paper<sup>1</sup> on the radioactivity of thorium compounds we showed that, in the case of minerals, when the activity due to uranium was deducted, the remaining activity was strictly proportional to the percentage of thorium present. The following table, taken from the earlier paper, summarizes the results obtained:

TABLE I.

No.	Name	% Th	% U	$k_m$	$k_U$	$k_{Th}$	$\frac{k_{Th}}{P_{Th}}$
1	Orangite. ....	43.1	7.76	649	255	394	914
2	Thorite .....	46.6	6.26	664	205	459	985
3	Monazite. ....	5.27	0.33	60.2	10.9	49.3	935
4	" .....	15.18	0.46	164	15	149	982
5	" .....	2.72	0.12	29.8	4.0	25.8	950

Mean = 953

The symbol  $k_m$ , represents the specific activity of the mineral, in terms of the activity of 1 sq. cm. of a thick film of  $U_3O_8$  as unity;  $k_U$  is the activity due to uranium;  $k_{Th} = k_m - k_U$ .  $P_{Th}$  is the weight of thorium per gram of mineral.

Results similar to these were published by Boltwood<sup>2</sup> in the same number of the Am. J. Sci. as that in which our paper appeared. Boltwood's results were expressed in arbitrary units, but showed just as clearly as do those of Table I, the constant specific activity of thorium in minerals. A third simultaneous paper, in the same journal by Dandourian<sup>3</sup> contained similar conclusions reached as a result of a different method of investigation; which consisted in the measurement of the intensity of the excited activity obtained from the thorium emanation given off by solutions of minerals. These results were also expressed in arbitrary units.

In the first paper we stated:

"All of the thorium activity measurements, as well as those of uran-

<sup>1</sup> Am. J. Sci., 21, 433 (1906).

<sup>2</sup> Ibid., 21, 409 (1906).

<sup>3</sup> Ibid., 21, 427 (1906).

ium compounds and minerals, were made with a distance of 3.5 cm. between the active films and the charged electrode. While this thickness of air is sufficient to absorb practically all of the alpha rays of uranium, it is scarcely great enough to absorb completely the more penetrating alpha rays of some of the radium and thorium products<sup>1</sup>. With a greater distance than 3.5 cm. between the films and electrode a somewhat greater activity will be found for uranium and thorium minerals. The general relationship between the radioactivity and the composition of such minerals having now been fully established, we are starting a new series of measurements on minerals with the object of determining their activities under conditions such that the maximum ionizations due to the alpha rays can take place in the space between the film and the electrode." The recent work of Hahn<sup>2</sup> on the ranges of the products of thorium, also emphasizes the necessity of a larger ionization chamber than we first used.

In the new series of measurements, we worked in the manner described in the preceding paper on *The Specific Radioactivity of Uranium*, using the new electroscope, and films of the mineral deposited by sedimentation on flat, rimless plates. Since the earlier work had shown that the specific activity of thorium in its minerals is constant, it was considered unnecessary to repeat the activity measurements of more than three of the minerals in order to determine the exact value of this constant. The new results are given in Table 2. The new value found for the specific activity of uranium in minerals, 3616, was used in calculating the activity due to that element in each thorium mineral.

TABLE 2.

Name	% Th	% U	$k_m$	$k_U$	$k_{Th}$	$\frac{k_{Th}}{P_{Th}}$
Orangite.....	43.1	7.76	707	281	426	988
Thorite.....	46.6	6.26	699	226	473	1015
Monazite.....	15.18	0.46	172	16.6	155.4	1025
					Mean	1009

The mean value of  $k_{Th}/P_{Th}$ , 1009, is the specific activity of thorium containing the equilibrium amounts of its products.

We also previously found that the specific activity of thorium in pure  $ThO_2$  obtained in the analyses of minerals by Neish's process<sup>3</sup>, was constant and equal to the specific activity of thorium in minerals. But the activity of pure  $ThO_2$  prepared from commercial samples of pure nitrate was always much less than that obtained from minerals by Neish's process<sup>3</sup>. The lat-

<sup>1</sup> Rutherford, *Radioactivity*, p. 168, 1905; Bragg and Kleeman, *Phil. Mag.*, 10, 318 and 600 (1905).

<sup>2</sup> *Phil. Mag.*, 11, 794; 12, 82 (1906).

<sup>3</sup> *This Journal*, 26, 780 (1904).

<sup>4</sup> The activities were measured four or five weeks after preparation when the samples had regained the amounts of  $ThX$ , etc., corresponding to the amounts of radiothorium present in each case.

<sup>5</sup> Boltwood and Dadourian obtained similar results.

ter sort contained the maximum or equilibrium amount of radiothorium, while the former evidently did not. It seemed, therefore, as if the technical method of preparation of thorium nitrate was more effective in separating radiothorium from thorium than was Neish's analytical method. We therefore attempted, by various chemical processes, to remove from thorium the whole of the radiothorium, with the object in view of obtaining thorium of minimum activity. As previously announced, we were able by the application of certain processes, many times repeated, to reduce the permanent activity of thorium considerably below that of the least active commercial sample used. But, in spite of the apparently promising results of the preliminary experiments, we did not succeed in separating radiothorium completely from thorium. In fact, it now appears doubtful whether it is possible by chemical treatment to separate any radiothorium from thorium. In a recent paper,<sup>1</sup> Hahn has pointed out that the activity of thorium preparations decreased spontaneously to an appreciable extent in the course of a few years; Boltwood<sup>2</sup> has also observed the same thing. We are able to confirm these observations by new measurements of the activity of preparations made and first measured about one and one-half years ago. Hahn also found thorium preparations nine to 12 years old were more active than those three years old. These facts are explained by Hahn by the supposition that there is an inactive product, which he has called mesothorium, between thorium and radiothorium and that this intermediate product is removed in the process of preparation of pure compounds from minerals; but that the radiothorium remains with the thorium. Hahn first estimated the period of mesothorium to be about seven years; in his second paper<sup>3</sup>, he states that his estimate is apparently somewhat too high, but in neither paper does he give the numerical data upon which the estimate is based. According to Blanc<sup>4</sup>, the period of radiothorium is 737 days. The low activity of commercial samples of thorium, as observed by Boltwood and by Dadourian, as well as by ourselves, is explained by Hahn as due to the decay of radiothorium with time, rather than to its removal by chemical processes. It is also probable that the decrease in activity of thorium preparations, which we observed after numerous chemical treatments, was the result solely of the decay of radiothorium, (aided by the chemical removal of mesothorium), during the time which had elapsed between the measurements of activity which preceded and those which followed the chemical treatments; in fact our experiments strongly indicate that radiothorium is entirely inseparable from thorium by chemical processes. Of course the indirect

<sup>1</sup> Ber., 40, 1462 (1907).

<sup>2</sup> Am. J. Sci., 24, 93 (1907).

<sup>3</sup> Ber., 40, 3304 (1907).

<sup>4</sup> Physik. Z., 8, 321 (1907).

separation of radiothorium may doubtless be accomplished by the removal, from time to time, of the mesothorium; the radiothorium will then continue to decay until in the course of 15 or 20 years it has practically completely disappeared.

We found, as shown in our first paper on this subject, that thorium dioxide obtained in the analyses of minerals by Neish's method had the same activity as it had in the original mineral. Neish's process involves one precipitation with oxalic acid; one with potassium hydroxide; and two with nitrobenzoic acid. Boltwood found similar results with thorium dioxide obtained from minerals by analytical processes in which the thorium was separated either by means of repeated treatments with ammonium oxalate or repeated precipitations with sodium thiosulphate. It follows from these results that none of the chemical processes involved removes any appreciable fraction of the radiothorium.

We have made a number of additional experiments in which commercial samples ("A" and "B") of thorium nitrate<sup>1</sup> have been subjected to the various treatments described below and finally converted into thorium dioxide.

(1). Twenty grams of sample A were dissolved in 200 cc. of boiling water and a solution containing one gram of oxalic acid was added; this precipitated about one-eighth of the thorium. The oxalate so obtained was converted into oxide by ignition.

(2). Additional one gram portions of oxalic acid were added to the filtrate from (1), the precipitate being filtered out after each addition; the eighth precipitate was ignited to oxide and constituted sample 2.

(3). Ten grams of sample A were dissolved in 300 cc. of boiling water and precipitated with 12 g. of sodium thiosulphate in 100 cc. of water. The boiling was continued one or two minutes. The precipitate was filtered out and dissolved in dilute nitric acid, the excess of the latter was nearly neutralized with ammonia and the whole process repeated. After eight precipitations in this manner the material was converted into oxide.

(4). Five grams of sample A were dissolved in 200 cc. of water and precipitated, at boiling temperature, with five grams of potassium chromate in 50 cc. of water. The precipitate was filtered out and dissolved in dilute nitric acid; the solution was diluted and the thorium chromate again precipitated from the hot solution by the addition of ammonia. The solution was acid, in reaction, at the end of the precipitation. After eight precipitations in this way, the solution in nitric acid was treated with an excess of oxalic acid; the oxalate was washed and converted into oxide.

<sup>1</sup> The samples were made by the firm of C. A. F. Kahlbaum; the oxide obtained by ignition was analyzed by Neish's method and found to be practically chemically pure in each case.

(5). Two grams of the sample A and 10 g. of barium chloride were dissolved in 200 cc. of water and a solution of 6.5 g. of ammonium oxalate was added; this was just sufficient to precipitate both the thorium and the barium as oxalates. Another portion of 6.5 g. of ammonium oxalate was now added to dissolve the thorium as double oxalate. After being heated to boiling, the residue of barium oxalate was filtered out and the filtrate was treated with 10 g. more of barium chloride. This process was repeated until 7 precipitations had been made. The barium oxalate was removed from the last precipitate by means of dilute hydrochloric acid; the thorium oxalate remaining was converted into oxide by Neish's method.

(6). Ten grams of sample A were dissolved in 400 cc. of water and precipitated with an excess of freshly distilled ammonia. The separated precipitate was dissolved in nitric acid and the process repeated 100 times; the last precipitate was converted into oxide. Analysis showed that this oxide contained 4.6 per cent. of impurity, due to the action of the alkaline solutions on the glass vessels used.

(7). Twenty grams of solid nitrate, sample B, were ground in a mortar with an excess of concentrated ammonia; the hydroxide so formed was filtered out, and ignited to oxide. The oxide so obtained is much more compact than that formed by the direct ignition of the nitrate.

(8). Fifteen grams of sample B were dissolved in 300 cc. of water and precipitated with hydrogen peroxide, at a temperature of about 70°. The separated precipitate was dissolved in nitric acid; the thorium was again precipitated from the dilute solution by the addition of 45 g. of ammonium acetate and 35 cc. of hydrogen peroxide. The whole process was repeated until 40 precipitations had been made; the last precipitate was purified by Neish's method and converted into oxide.

The activities of these preparations were measured in the old way (films in tins with rims and 4.5 cm. between films and electrode), but the results as given in Table 3 have been multiplied by the factor 1.12, which is the ratio of the activity as determined in the new way (flat films and 8.5 cm. ionization space) to that determined in the old.

TABLE 3—ACTIVITIES OF SAMPLES OF THORIUM DIOXIDE.

Chemical treatment	Date of precipitation. Oxides from sample A	Activity on May 8th, 1906	Activity on September 12th, 1907
1. 1 pptn. oxalic acid.....	Apr. 6, 1906	529	417
2. 8 pptn. oxalic acid.....	Apr. 6, 1906	529	423
3. 8 pptn. thiosulphate.....	Apr. 4, 1906	529	414
4. 8 pptn. chromate.....	Apr. 9, 1906	547	421
5. 7 pptn. barium oxalate....	June 11, 1906	...	420
6. 100 pptn. ammonia.....	Apr. 3, 1906	510 <sup>1</sup>	402 <sup>1</sup>
	Oxides from sample B		
7. 1 pptn. ammonia.....	Nov. 11, 1905	Feb. 24, 1906	Sept. 12, 1907
8. 40 pptn. hydrogen peroxide	June 28, 1906	477	410
		...	385

<sup>1</sup> The values given have been corrected for the 4.6% impurity contained in the sample.

As has been shown, one precipitation with oxalic acid, (which is included in Neish's analytical method), does not remove any radiothorium from thorium. Since the activities of samples (2) to (5) were practically the same as that of sample (1) at each time of measurement, as shown in Table 3, it follows that none of the processes used in making these samples effects any separation of radiothorium. The activity of sample (6) is a little low, but the difference, about 4 per cent., may be only experimental error; at most since there were 100 precipitations, one precipitation with ammonia removes but 0.04 per cent. of the radiothorium present. It would seem from a comparison of the activities of (7) and (8) that 40 precipitations with hydrogen peroxide remove a small portion of the radiothorium; yet the lower activity of (8) may be due to a different cause: the incomplete removal of mesothorium from (7) at the time of its preparation from the nitrate Nov. 11, 1905. This point will be considered further in subsequent paragraphs. The isolation of radiothorium from thorianite<sup>1</sup> and from pure thorium nitrate<sup>2</sup> seems to indicate the possibility of separating radiothorium by chemical processes; but these results may have been accomplished through the separation of mesothorium, which in time changed spontaneously into radiothorium.

The specific activities given in Table 3 refer to thoria containing the amounts of ThX and subsequent products, corresponding to the amounts of radiothorium in the samples, since the activity measurements were made about one month after the last chemical treatment. As most of the chemical processes, used in the attempts to remove radiothorium, readily remove ThX, the activity of any sample immediately after its preparation was much less than one month later. Rutherford and Soddy<sup>3</sup>, who were the first to observe this fact in the case of thorium precipitated with ammonia, found that the final activity was about 4 times as great as the initial. We found the ratio of final to initial activity to be approximately 2.5 for the various samples of thoria prepared from sample A of nitrate.

The corresponding ratio for thoria separated from minerals in analyses by Neisl's method was about 3.2. The greater ratio in the case of thoria rich in radiothorium was observed by us at the time of the measurements made in May, 1906, Table 3, and was considered, at that time, to prove conclusively that thorium itself is active. And, although the available data were not exact, we estimated that the specific activity of thorium dioxide alone was probably between 100 and 130. Hahn, in his recent paper already referred to, has observed the greater ratio of maximum to minimum activity for samples rich in radiothorium and has pointed out that this shows finally and conclusively that thorium itself is active, that

<sup>1</sup> Ramsay, *J. chim. phys.*, 3, 617 (1905); Hahn, *Ber.*, 38, 3371 (1905).

<sup>2</sup> Blanc, *Physik. Z.*, 7, 620 (1906).

<sup>3</sup> *Phil. Mag.*, Sept., 1902.

is, that thorium alone emits  $\alpha$ -rays. We do not wish to make any claim of priority on this point, as this is the first publication of our observations; but we do wish to emphasize the fact that Hahn's conclusion is correct.

As was just stated, the data from which we first estimated the activity of thorium alone were not exact; this was due to the fact that the numerous precipitations with ammonia required for the removal of ThX and its products<sup>1</sup> introduced silica and other impurities from the glass. An improved method for the separation of ThX and all subsequent products from thorium has been worked out by Mr. G. C. Ashman and one of us.<sup>2</sup> It was found that precipitation of thorium with meta-nitrobenzoic acid leaves ThX and ThA in the solution; four precipitations at intervals of two hours give finally chemically pure thorium dioxide, which is entirely free from ThX and its subsequent products. From the observations of the minimum and maximum activities of the two samples of thorium, one containing but little radiothorium, the other freshly prepared from a mineral, the specific activity of thorium dioxide, free from radiothorium and all other active products, was found to be 105. The activities of the equilibrium amounts of radiothorium and of ThX and subsequent products for one gram of thorium dioxide were 182 and 655 respectively. These values refer to flat films and an ionization space of 8.5 cm. between the film and the electrode, the measurements having been made in the electroscope described in the preceding paper.

If the chemical processes involved in the preparation, from a mineral, of any sample of a pure thorium compound remove all or part of the mesothorium, the activity of the sample will fall to a minimum, in the course of time, and then increase again, as Hahn has stated. It follows also that this minimum activity will be *perfectly definite*, provided the whole of the mesothorium is removed and that the purification processes are all carried out at one time, say within a period of one month. The ratio of this minimum activity to the activity of thorium containing the equilibrium amounts of all its products is a fraction, which is a function of (1) the period of mesothorium; (2) the period of radiothorium; (3) the activity of thorium alone; (4) the activity of thorium and its subsequent products. Conversely, if the value of this minimum be known, the period of mesothorium may be calculated, since all of the other data are now available.

Rutherford<sup>3</sup> has developed the general equation for the variation with time of the number of particles of one radioactive body, produced by the disintegration of another. This equation applies to the formation of

<sup>1</sup> Rutherford and Soddy, Loc. cit.

<sup>2</sup> The results will be published soon.—H. N. McCoy.

<sup>3</sup> Radioactivity, 331, (1905).

radiothorium from mesothorium. Let  $\lambda_1$  and  $\lambda_2$  represent the disintegration constants and  $n_0'$  and  $n_0''$  the equilibrium numbers of particles per gram of thorium dioxide, of mesothorium and radiothorium respectively. The number of particles,  $n''$ , of radiothorium formed in time,  $t$ , from  $n_0'$  particles of mesothorium, which contained no radiothorium at time zero, is given by equation (1)

$$n'' = \frac{n_0' \lambda_1}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (1)$$

But

$$n_0' \lambda_1 = n_0'' \lambda_2$$

Therefore

$$n'' = \frac{n_0'' \lambda_2}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (2)$$

If, from a quantity of thoria which contained the equilibrium amounts of all its products, the mesothorium only were removed completely at time zero, then  $(n_0'' - n'')/n_0''$  would represent the fraction of the equilibrium number of particles of radiothorium left in the thoria at the time,  $t$ . The fraction,  $(n_0'' - n'')/n_0''$ , decreases with time and reaches a minimum, which may be called  $m$ , at a time which depends only on the periods of the two substances concerned. If we take the activity of one gram of thorium dioxide alone as 105 and the activity of the equilibrium amounts of its products as 837 the minimum specific activity of the thoria, corresponding to a minimum content of radiothorium, is equal to  $837m + 105$ .

We have found that the present activity of a sample of thoria, made by strongly igniting sample A of thorium nitrate, is 476. If we take this activity as the minimum, we may write  $837m + 105 = 476$ ; from which  $m = 0.443 = (n_0'' - n'')/n_0''$ . From this last relationship and equation (2), the value of  $\lambda_1$  may be found; and from  $\lambda_1$  the period of mesothorium. The value thus found for the last mentioned constant was 5.4 years; it may actually be greater, however, since the minimum activity may be less than 476. If the period is 5.4 years, the minimum activity will be reached in  $4\frac{1}{2}$  years from the date of preparation. Since the specific activity of this sample was 579 on Dec. 8, 1905, it was then probably about 2.0 years old. If so, it is now, Sept., 1907, about 3.8 years old; and although the minimum activity will not be reached for 9 or 10 months (assuming the period of mesothorium to be 5.4 years) the total activity will diminish less than one per cent. in this time. From these considerations it seems probable that the period of mesothorium is not far from 5.5 years. If so, the minimum activity will be reached in 4.6 years. This conclusion is in good agreement with the changes of activity of samples which have been under observation for about  $1\frac{1}{2}$  years.

On April 4th to 9th, 1906, samples (1) to (4), Table 3, were subjected to chemical treatment which probably removed all of the mesothorium



present at that time. The mean activity of these samples was 534 on May 8, 1906, and 418 on Sept. 12, 1907. In the interval, 492 days, the radiothorium present on May 8th, 1906, would decay to  $e^{-492\lambda_2} = 0.630$ ; the products of radiothorium would disappear in the same proportion. Now the specific activity of thorium dioxide itself is 105. If no radiothorium had been formed from the new mesothorium produced from thorium during the interval of about 525 days between the date of preparation and that of final measurement, Sept. 12, 1907, the activity of the samples would have been  $0.630(534 - 105) + 105 = 375$  on the latter date. But some radiothorium must have been produced from the mesothorium formed from thorium during this interval and it is easy to show that the activity of the radiothorium so formed would be, for  $t = 525$ ,

$$837 \left\{ 1 - \left[ \frac{\lambda_2}{\lambda_2 - \lambda_1} \left( e^{-\lambda_1 t} - e^{-\lambda_2 t} \right) - e^{-\lambda_2 t} \right] \right\} = 30.$$

The calculated specific activity on Sept. 12, 1907, of samples 1 to 4 is, therefore,  $375 + 30 = 405$ . The observed activity was 418.

Table 4 gives a summary of the results, of a similar sort, obtained with other samples already described as well as with two additional samples, 9 and 10.

Sample 9 was thorium dioxide prepared by Neish's method from a sample of "partially purified oxalates," made by the Welsbach Light Company.<sup>1</sup>

Sample 10 was thorium dioxide obtained in the analyses of orangite and thorite<sup>2</sup>.

TABLE 4.

Samples	Date of Preparation	Date and Activity	Date and Activity	Calculated Activity
1-2-3-4	Apr. 4-9, 1906	May 8, 1906; 534	Sept. 12, 1907; 418	405
6	" 3, "	" " " 510	" " " 402	390
7	Nov. 11, 1905	Feb. 24, " 477	" " " 410	370
9	May 8, 1906	July 6, " 854	" 23 " 610	625
10	Dec. 2-6, 1905	Feb. 9, " 947	" 28 " 621	630

With the exception of the results for sample (7), the values calculated and observed are in fairly good agreement. The higher observed activity of (7) is very probably due to incomplete removal of mesothorium at the time of the preparation of the oxide from the nitrate, Nov. 11, 1905; since the chemical treatment consisted only in grinding the solid nitrate with concentrated ammonia, filtering and igniting. The difference in activity of (7) and (8), Sept., 1907, (Table 3) may also be due to the incomplete separation of mesothorium from (7), rather than to the removal from (8) of part of the radiothorium by the chemical treatment employed.

<sup>1</sup> We wish to express our thanks to Mr. H. S. Miner, chemist for the Welsbach Company, who has supplied us with this as well as a number of other samples of thorium products.

<sup>2</sup> See Table XIV, Am. J. Sci., 21, 443 (1906).

On the other hand, it is very probable that the chemical processes carried out in the preparation of all the other samples, removed practically all of the mesothorium contained in them. Thus the activity of a sample of thorium dioxide, made by ignition alone of sample A of nitrate, had an activity of 476 in Sept., 1907, while samples 1 to 4, made from the same sample of nitrate, had a mean activity of 418.

### Summary

1. The specific activity of thorium in minerals was found to be 1009 (the unit being the activity of one sq. cm. of a thick film of  $U_3O_8$ ) when measured under such conditions that all of the  $\alpha$ -rays reach their maximum ranges in air.

2. The direct separation of radiothorium, from thorium by chemical processes is remarkably difficult, if not impossible. This question is being studied further in this laboratory.

3. The diminutions of activity of thorium, which we previously observed after certain chemical treatments, are completely explained by Hahn's hypothesis of an intermediate product, mesothorium, between thorium and radiothorium; which product is easily removed by the chemical treatments; in consequence of which the radiothorium decays with time and thus causes the observed changes of activity.

4. If all of the mesothorium be removed, at one time, in the process of preparation from a mineral of pure thorium dioxide, the activity of the latter will fall to a definite minimum. From the activity of a sample of thoria, supposed to have reached this minimum, the period of mesothorium was calculated to be 5.5 years.

5. The quantitative changes of activity with time, of a number of samples of thoria agreed well with the values calculated on the assumption of a period of 5.5 years for mesothorium.

Oct. 12, 1907.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BUREAU OF STANDARDS, No. 3].

### THE ATOMIC WEIGHT OF HYDROGEN.

BY WILLIAM A. NOYES.

Received September 10, 1907.

Some years ago the writer<sup>1</sup> carried out a series of determinations of the quantitative composition of water, from which the value 15.896 was calculated for the atomic weight of oxygen on the hydrogen basis. The opinion was expressed, in the paper, that the true value was probably within one part in a thousand of this number, and that it was rather below than above the value reported. Several years later Morley<sup>2</sup> pub-

<sup>1</sup> Am. Ch. J., 12, 441 (1890).

<sup>2</sup> Smithsonian Contributions to Knowledge, 1895 : Am. Ch. J., 17, 267 and 396 ; Z. physik. Chem., 17, 87.