silver and gold in the nitrate which was prepared from undistilled tellurium. The results given above, which were obtained with a sample of nitrate which had been purified by crystallization alone, are practically identical with those obtained from a sample of nitrate prepared from the oxide which had been five times distilled.

The results obtained with the nitrate prepared from the tellurium which had been converted into the telluropentathionate are recorded in experiments numbered 4, 5 and 6. In the experiment numbered 7 the nitrate used was prepared from a sample of oxide which had been distilled but once, while in experiments 8 and 9 the oxide from which the nitrate was made had been distilled five times. In numbers 10, 11 and 12 are recorded the results of the analyses of samples of nitrate prepared from the residue from the first distillation. If the dvitellurium of Mendeléeff had been present, the atomic weight of this fraction should have been much higher than 127.48.

The results show clearly that the application of the methods studied effected no decomposition of tellurium. As these methods would have shown the presence of an unknown element with the properties which have been assigned to dvitellurium by Mendeléeff, the conclusion can be drawn that no such element is present. The work adds to the experimental evidence in favor of the elementary nature of tellurium.

The atomic weight found agrees well with the most reliable values, which have been determined by others.

SIMMONS COLLEGE, BOSTON, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE CARRYING DOWN OF AMMONIUM OXALATE BY OXALATES OF THE RARE EARTHS.

BY GREGORY PAUL BAXTER AND ROGER CASTLE GRIFFIN.

Received October 10, 1906.

A RAPID and convenient method for approximate atomic weight determinations of the trivalent metals of the rare earths is the "permanganate" method, in which the ratio $M_2O_3 : 3C_2O_3$ is determined. In this process a known weight of the oxalate of the rare earth is ignited to oxide and the latter is weighed. Then a known weight of the same sample of oxalate is dissolved in sulphuric acid and the oxalic acid is titrated with standard potassium permanganate. By dividing the ratio $\frac{M_2O_3}{M_2(C_2O_4)_3}$ found in the first process by the ratio $\frac{3C_2O_3}{M_2(C_2O_4)_3}$ found in the second, the ratio $\frac{M_2O_3}{3C_2O_3}$ is determined, from which the atomic weight may be calculated.[1]

It has already been pointed out by Gibbs[2] and others that the oxalates of the rare earths contain varying amounts of water, and that it is very necessary to grind thoroughly the whole specimen of oxalate which is to be used for analytical purposes, in order to ensure homogeneity of material. Furthermore, the fact has long been recognized that in the presence of potassium or sodium oxalates some of these substances may be carried down by the insoluble oxalates. Large discrepancies in the observed atomic weight as determined by the above method, with material which had been precipitated by oxalic acid or ammonium oxalate, led to the following research upon the effect of varying conditions upon the composition of the oxalates of certain of the rare earths. It is found that ammonium oxalate also, but not oxalic acid, may be carried down in considerable quantities by the rare earth oxalates.

Neodymium was the first element studied. A specimen of oxalate was ignited to oxide and dissolved in a considerable excess of nitric acid. The absorption spectrum of the solution showed the bands of neodymium only. A portion of the solution was then slowly added, with constant stirring, to a solution of a large excess of oxalic acid. The resulting oxalate was washed ten times by decantation with hot water and collected on a porcelain Gooch crucible, provided with a disk of filter-paper instead of asbestos. On testing the filtrate the precipitation of the neodymium was found to be complete. After the oxalate had been dried in an electric air-bath at 120–130° for about twenty hours, it was thoroughly mixed by grinding in a porcelain mortar.

---

[1] This method was first proposed by Stolba: Sitzber. böhm. Ges., Dec. 1878; Also Chem. News, 41, 31 (1880).

[2] Pr. Am. Acad. 28, 262 (1893).

Portions of about 0.5 gram were then transferred from a weighing-bottle to weighed platinum crucibles, and the crucibles were ignited, first in a Bunsen flame, and finally for several minutes with a blast-lamp. The crucibles were allowed to cool in desiccators and were again weighed. In each case a repetition of the ignition failed to change the weight of the oxide.

Next, portions of from 0.2 to 0.3 of a gram of the oxalate were weighed into Erlenmeyer flasks, and after the addition of about 5 cc. of concentrated sulphuric acid diluted with fifty of water, the flasks were heated on the steam-bath until the oxalate was completely dissolved. Then the oxalic acid was determined by titration with potassium permanganate solution. This solution was standardized with oxalic acid which had been allowed to come to constancy over sulphuric acid of the sp. gr. 1.35. The oxalic acid had been many times recrystallized, first from hydrochloric acid solution, then from pure water until free from chlorides.

Since the weight of oxalate found experimentally was considerably less than 100 per cent., as a check on the process the water content was determined by igniting weighed portions of the oxalate in a porcelain boat in a current of dry air, and absorbing the water in a weighed phosphorus pentoxide tube.

The results of the complete analysis are as follows:

	I.	II.	III.	Average.
Weight of oxalate.................	0.6505	0.5938	0.5865	
Weight of Nd_2O_3.................	0.3182	0.2908	0.2869	
Per cent. of Nd_2O_3.................	48.92	48.97	48.92	48.94
Weight of oxalate.................	0.3164	0.3230	0.2613	
Vol. of $KMnO_4$ sol..............	28.03	28.60	23.16	

1 cc. $KMnO_4 = 0.003547$ gram C_2O_3.

	I.	II.	III.	Average.
C_2O_3 calculated.....................	0.0994	0.1014	0.0822	
Per cent. of C_2O_3.................	31.43	31.41	31.44	31.43
Weight of oxalate.................	0.6575	0.6264		
Weight of water...................	0.1278	0.1241		
Per cent. of water.................	19.44	19.81		19.62
			Total,	99.99

$$\text{Ratio } M_2O_3 : 3C_2O_3 = \frac{48.94}{31.43} = 1.5571$$

$$M = 144.2 \qquad (Nd = 143.6)$$

The observed value for the atomic weight of neodymium is sa near the most probable value of this constant as the purity of the sample would lead one to expect. Since the oxalate used in the above experiments was precipitated with a very large excess of oxalic acid, the possibility existed that some of the precipitant had been carried down by the precipitate. In order to determine whether this was the case, another sample of the same material was precipitated in a similar manner, but with a very slight excess of oxalic acid.

	I.	II.	III.	Average.
Per cent. of Nd_2O_3	58.02	57.98	57.94	57.98
Per cent. of C_2O_3	37.25	37.27	37.17	37.23

$$\text{Ratio } M_2O_3 : 3C_2O_3 = \frac{57.98}{37.23} = 1.5573.$$

$$M = 144.2 \qquad (Nd = 143.6)$$

The agreement of the values for the atomic weight of neodymium obtained from the analyses of oxalate which had been precipitated with a very large and with a slight excess of oxalic acid shows conclusively that no appreciable tendency for the carrying down of oxalic acid exists.

Precipitation by means of ammonium oxalate was next investigated. A solution of neodymium oxide in nitric acid was nearly neutralized with ammonia, and was added to a slightly ammoniacal solution of a small excess of ammonium oxalate. Precipitation was found to be complete. After the precipitation the supernatant liquid was faintly acid. By adding the neodymium solution to the oxalate, occlusion, if it exists at all, is to be expected to be at a maximum. The oxalate was thoroughly washed, dried and powdered. Then it was analyzed as before.

	I.	II.	III.	Average.
Per cent. of Nd_2O_3	50.65	50.58	50.70	50.64
Per cent. of C_2O_3	37.99	38.01	38.02	38.01
Per cent. of H_2O	11.28	11.22		11.25
			Total,	99.90

$$\text{Ratio } M_2O_3 : 3C_2O_3 = \frac{50.64}{38.01} = 1.3322$$

$$M = 119.9 \qquad (Nd = 143.6)$$

Since it was certain from these results that the salt contained too much oxalate, and since it was probable that the excess was due to ammonium oxalate which had been carried down by the neodymium oxalate, a portion of the precipitate was tested for ammonia, after solution in nitric acid, by adding an excess of potassium hydroxide. Ammonia was evolved in quantity. It was evident, therefore, that ammonium oxalate is carried down by neodymium oxalate to a considerable extent. The determination of the water in this oxalate includes the ammonia as well as the water. However, since ammonium oxalate, when heated, breaks up partially into cyanogen and water, this determination is slightly in error. During the analysis of the oxalate for water the odor of cyanogen was perceptible.

Neodymium oxalate, which had been precipitated by addition to a nearly saturated solution of ammonium oxalate, was found to contain a still larger proportion of ammonium oxalate.

	I.	II.	III.	Average.
Per cent. of Nd_2O_3	49.56	49.70	49.59	49.62
Per cent. of C_2O_3	39.63	39.66	39.66	39.65
Per cent of $H_2O + NH_3$	9.91	10.31		10.11
			Total,	99.38

$$\text{Ratio } M_2O_3 : 3C_2O_3 = \frac{49.62}{39.65} = 1.2514$$

$$M = 111.2 \qquad (Nd = 143.6)$$

Upon the assumption that the average atomic weight of the metals in this sample is 144.2, the amount of C_2O_3 corresponding to 49.62 per cent. of oxide is 31.86. The difference between this proportion and that observed is 7.79, which in turn corresponds to 3.68 per cent. of ammonia. In order to determine whether this proportion of ammonia actually existed in the oxalate, the latter was analyzed for ammonia. Weighed portions of the oxalate were dissolved in dilute sulphuric acid and the solutions were diluted to about one-half liter. Then they were transferred to a liter retort, into the tubulature of which was fitted a dropping funnel containing a strong solution of ammonia-free potassium hydroxide. The potassium hydroxide was slowly added to the solution in the retort and the ammonia set free was distilled into standard hydrochloric acid in the usual way. Blank tests were made and slight corrections were applied. The percentage of ammonia obtained experimentally agrees very closely with that calculated above.

	I.	II.	III.	IV.	Average.
Weight of oxalate	0.4343	0.2872	0.3290	0.3098	
cc. $N/_{10}$ HCl used	9.22	6.10	6.76	6.46	
Per cent. of ammonia	3.61	3.62	3.55	3.55	3.58
				Calculated,	3.68

Next, precipitation in neutral solution with ammonium oxalate was investigated. A solution of neodymium chloride as nearly neutral as possible was prepared by evaporating to dryness on the steam-bath a solution of the oxide in hydrochloric acid, and repeating the evaporation several times after dissolving the residue in water. This solution was added drop by drop with continual agitation to a concentrated hot solution of ammonium oxalate. Occlusion is to be expected to the same extent here as in the previous case. Such proved to be the result.

	I.	II.	III.	Average.
Per cent. of Nd_2O_3	49.57	49.49		49.53
Per cent. of C_2O_3	39.25	39.24	39.25	39.25
Per cent. of $H_2O + NH_3$	11.28	11.74		11.51
			Total,	100.29
Per cent. of NH_3	3.50	3.50		3.50
Per cent. of C_2O_3 corresponding to NH_3				37.41
Per cent. of C_2O_3 corresponding to Nd_2O_3				31.84

$$\text{Ratio } M_2O_3 : 3C_2O_3 = \frac{49.53}{31.84} = 1.5555$$

$$M = 144.0 \qquad \text{Theoretical} = 144.2$$

It has been pointed out by Richards that occlusion of any substance is proportional to the concentration of that substance in the molecular condition at the moment of precipitation.[1] In the present instance, since ammonium oxalate is the substance occluded, occlusion should increase with increasing concentration of molecular ammonium oxalate at the moment of precipitation. This has already been found to be the case when precipitation is carried out in neutral or very nearly neutral solution. In a solution containing much strong acid, however, the concentration of molecular ammonium oxalate would be very low, for the reaction between the hydrogen ion and the oxalate ion is nearly complete, even when the hydrogen ion concentration is not large. In the case of nitric acid the equilibrium with ammonium oxalate may be represented as follows:

$$\begin{tikzcd}
2NH_4^{+} & + & C_2O_4^{=} \arrow[r, leftrightarrows] & (NH_4)_2C_2O_4 \\
+ & & + & \\
2NO_3^{-} \arrow[d, shift left, rightarrow] & + & 2H^{+} \arrow[r, leftrightarrows] \arrow[d, shift left, rightarrow] & 2HNO_3 \\
2NH_4NO_3 \arrow[u, shift left, rightarrow] & & H_2C_2O_4. \arrow[u, shift left, rightarrow] &
\end{tikzcd}$$

If then neodymium oxalate is precipitated by ammonium

---

[1] Pr. Am. Acad. 35, 377; 36, 377.

oxalate in the presence of much nitric acid, little or no carrying down of ammonium oxalate is to be expected.

In the next experiment neodymium nitrate was added to a hot, nearly saturated solution of ammonium oxalate containing a large amount of nitric acid. The precipitate was washed with hot water, dried, powdered and analyzed as before. The analysis of the precipitate confirms the prediction made above. The precipitate contained a mere trace of ammonia, which may account for the slight difference between the observed and theoretical results.

	I.	II.	Average.
Per cent. of Nd_2O_3	52.73	52.73	52.73
Per cent. of C_2O_3	33.90	33.91	33.91
Per cent. of H_2O	12.39	12.53	12.46
		Total,	99.10

$$\text{Ratio } M_2O_3 : 3C_2O_3 = \frac{52.73}{33.91} = 1.5551$$

$$M = 144.0 \qquad \text{Theoretical} = 144.2$$

Praseodymium oxalate also was studied in the same way. To a solution of praseodymium nitrate containing nitric acid, an excess of oxalic acid solution was added, drop by drop, with continual agitation. The oxalate was thoroughly washed with water, dried in an air-bath, powdered in a mortar and analyzed as in the case of neodymium. The oxalate, upon ignition, was eventually converted into a black oxide, of the composition Pr_4O_7.[1]

	I.	II.	III.	IV.	Average.
Ratio Pr_4O_7 : oxalate	58.50	58.56			58.53
Per cent. of Pr_2O_3	57.12	57.17			57.15
Per cent. of C_2O_3	37.41	37.24	37.17	37.23	37.26
Per cent. of H_2O	6.42	6.23			6.33
				Total,	100.74

$$\text{Ratio } Pr_2O_3 : 3C_2O_3 = \frac{57.15}{37.26} = 1.5338$$

$$Pr = 141.7 \qquad \text{Theoretical} = 140.5$$

The difference between the experimental and theoretical values for the atomic weight of praseodymium may be due to uncertainty either as to the purity of the material employed or as to the composition of the oxide formed by ignition of the oxalate.

A solution of the same praseodymium material containing only a very slight excess of nitric acid, was then precipitated by

---

[1] Dammer: Handb. der anorg. Chem. 3, 42.

addition to a hot concentrated slightly ammoniacal solution of ammonium oxalate. Precipitation was complete. The precipitate contained very nearly as much ammonia as neodymium oxalate when precipitated under the same conditions.

	I.	II.	III.	Average.
Ratio Pr_4O_7 : oxalate	50.48	50.53		50.51
Per cent. of Pr_2O_3	49.28	49.33		49.31
Per cent. of C_2O_3	38.98	39.01		39.00
Per cent. of NH_3	3.45	3.40	3.45	3.43
Per cent. of C_2O_3 corresponding to 3.43 per cent. of NH_3				7.27
Per cent. of C_2O_3 corresponding to Pr_2O_3				31.73

$$\text{Ratio } M_2O_3 : 3C_2O_3 = \frac{49.31}{31.73} = 1.5541$$

$$M = 143.8 \qquad \text{Theoretical} = 140.5$$

The yttrium material employed proved to be far from pure, the atomic weight determined with the precipitate from acid solution being 102.9, while the atomic weight of yttrium is 89.0. Yttrium oxalate was precipitated by adding a solution of a slight excess of oxalic acid to an acid solution of the nitrate, and by adding a nearly neutral solution of the nitrate to a large excess of ammonium oxalate. The precipitate formed in the latter fashion proved to contain considerable ammonia, but when a correction is applied for this ammonia, both precipitates yield nearly the same result for the atomic weight of the sample.

ACID PRECIPITATION.

	I.	II.	Average.
Per cent. of Y_2O_3	46.24	46.31	46.28
Per cent. of C_2O_3	39.37	39.39	39.38
Per cent of H_2O	14.48	14.64	14.56
		Total,	100.22

$$\text{Ratio } M_2O_3 : 3C_2O_3 = \frac{46.28}{39.38} = 1.1750$$

$$M = 102.9$$

NEUTRAL PRECIPITATION WITH AMMONIUM OXALATE.

	I.	II.	Average.
Per cent. of Y_2O_3	41.22	41.25	41.24
Per cent. of C_2O_3	44.84	44.97	44.91
Per cent. of NH_3	4.54	4.53	4.53
Per cent. of C_2O_3 corresponding to 6.95 per cent. of NH_3			9.59
Per cent. of C_2O_3 corresponding to Y_2O_3			35.32

$$\text{Ratio } M_2O_3 : 3C_2O_3 = \frac{41.24}{35.32} = 1.1674$$

$$M = 102.1$$

The last material investigated was separated from a solution of the rare earths contained in Texas gadolinite by means of fractional precipitation with magnesium oxide. The spectroscope showed it to be rich in erbium, and to contain samarium, while didymium was entirely absent. A portion of the oxalates was soluble in an excess of ammonium oxalate in neutral solution, although in acid solution precipitation was complete, hence undoubtedly ytterbium was present. In order to make certain that the same material was treated both in neutral solution and in acid solution, precipitation with ammonium oxalate in neutral solution was carried out first, and then, after the precipitate had been analyzed, the same material was dissolved and precipitated with oxalic acid in the presence of considerable nitric acid.

ACID PRECIPITATION.

	I.	II.	III.	Average.
Per cent. of M_2O_3	54.64	54.63	54.63	54.63
Per cent. of C_2O_3	34.94	34.94	34.96	34.95

$$\text{Ratio } M_2O_3 : 3C_2O_3 = \frac{54.63}{34.95} = 1.5633$$

$$M = 144.9$$

NEUTRAL PRECIPITATION WITH AMMONIUM OXALATE.

	I.	II.	Average.
Per cent. of M_2O_3	47.88	47.80	47.84
Per cent. of C_2O_3	40.05	40.04	40.05

$$\text{Ratio } M_2O_3 : 3C_2O_3 = \frac{47.84}{40.05} = 1.1945$$

$$M = 105.0$$

Per cent. of NH_3 (calculated. $M = 144.9$). 4.47

It is interesting to compute the relation of the number of molecules of the oxalates of the rare earths and of ammonia in the precipitates in which the ammonium oxalate content was at a maximum.

	Per cent. of oxide.	Per cent. of ammonia.	Per cent. of $(NH_4)_2C_2O_4$.	Molecules of $(NH_4)_2C_2O_4$ for one molecule $M_2(C_2O_4)_3$.
Nd_2O_3	49.62	3.58	13.05	0.71
Pr_2O_3	49.31	3.43	12.50	0.68
Y_2O_3	41.24	4.53	16.51	0.82
Er_2O_3(?)	47.84	4.47	16.29	0.93

The extent of the carrying down of ammonium oxalate by the rare earth oxalates which were investigated is much larger than in other cases of occlusion,[1] and leads to the conclusion that the

---

[1] Richards: Loc. cit.; Baxter: Am. Ch. J. 28, 298 (1902).

real cause of the phenomenon is not the formation of solid solutions of ammonium oxalate in the rare earth oxalates, as is the case with true occlusion, but the formation of a somewhat unstable double salt, possibly of the general formula $M_2(C_2O_4)_3(NH_4)_2C_2O_4$, analogous to the double salts with potassium and sodium oxalates. In either case the extent of the carrying down of ammonium oxalate by the insoluble oxalates would vary with the concentration of the molecular ammonium oxalate at the moment of precipitation.

SUMMARY.

(1) The results of the foregoing investigation show that the insoluble oxalates of neodymium, praseodymium, yttrium and certain other of the rare earths, exhibit a strong tendency to carry down ammonium oxalate, when precipitation takes place in neutral or nearly neutral solution.

(2) In the case of neodymium, it is shown that the amount of ammonium oxalate carried down is dependent upon the concentration of molecular ammonium oxalate at the moment of precipitation.

(3) Furthermore, it is shown that neodymium oxalate has no tendency to carry down oxalic acid, and that the occlusion of ammonium oxalate may be prevented by diminishing the molecular concentration of ammonium oxalate in solution by means of a strong acid.

It is probable that occlusion by other rare earth oxalates varies in the same way as in the case of neodymium.

(4) It is pointed out that the magnitude of the phenomenon is so great that the most reasonable explanation lies in the assumption of the existence of somewhat unstable double salts, rather than of true occlusion.

It seems probable also that the carrying down of the oxalates of sodium and potassium and of the other alkalies will vary with the conditions of precipitation as in the case of ammonium oxalate. This question is now under investigation in this laboratory.

CAMBRIDGE, MASS., Oct. 6, 1906.