## Summary and Conclusions.

The investigation of the conditions under which the ammonium molybdate test for stannous tin might be applicable to stannic solutions after reduction by zinc, showed:

1. That with a total acidity of 2.5 cc. of conc. hydrochloric acid in a volume of 10 cc., the acid being added as directed, the test is delicate to 0.01 mg. Sn in the absence of antimony.

2. That in the presence of 250 mg. of antimony the test can be used to detect 0.05 mg. of tin.

3. That the presence of 5 mg. of antimony is without influence on the delicacy of the test.

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# OBSERVATIONS ON THE RARE EARTHS.
## YTTRIUM CHLORIDE AND THE ATOMIC WEIGHT OF YTTRIUM.
### [PRELIMINARY PAPER.][1]

BY JAMES E. EGAN AND CLARENCE W. BALKE.

The results presented in this paper have been obtained in connection with a larger investigation upon the rare earths, which is being carried on in this laboratory.

Work is now in progress with material obtained from ten kilograms of gadolinite (from Norway), fifty-five kilograms of xenotime oxalate obtained from Drossbach & Company, Freiberg i. Saxony, fifteen kilograms of euxenite and ten kilograms of fergusonite, also large quantities of monazite residues furnished by the Welsbach Company, through the courtesy of Dr. H. S. Miner. The materials for the present work were obtained from the first two sources and the procedure for gadolinite and xenotime only will be given.

Ten kilograms of gadolinite were pulverized in a ball mill and then treated with an excess of concentrated hydrochloric acid with the addition of a little nitric acid from time to time. This was continued until decomposition was complete, and finally the mass was evaporated to dryness to dehydrate the silica. The residue was treated with water, the silica filtered off, and the rare earths precipitated from a slightly acid solution with oxalic acid. The oxalates were then washed by decantation.

Experience showed that the best and most rapid way to carry out an oxalic acid precipitation was to have both solutions hot. A small quantity of the acid was poured into the rare earth solution without stir-

ring, since the precipitate, which was in a viscous state, would gather into a large ball when stirred, which hardened and prevented thorough washing. After a few minutes the precipitate had solidified and the solution was stirred and an excess of oxalic acid added. A fine white precipitate was obtained which settled rapidly and was easily washed.

The xenotime oxalate was purchased as such from Drossbach and Company. It consisted principally of the earths of the yttrium group and contained but a small per cent. of the cerium earths.

## Methods of Fractionation.

The primary object of this investigation being the preparation of pure yttria, it was decided to attempt this by the combination of two methods. The two selected as the most suitable were the bromate methods of James[1] and a modification of the chromate method used by Muthmann and Böhn.[2]

The yttrium earths obtained from the two sources mentioned above were first subjected to fractionation as bromates and the process was carried out substantially as described, except that 750 cc. Jena flasks were found preferable to the casseroles used by Professor James. After the bromates had been fractionated until they had separated into well defined parts, portions which were richest in yttrium were removed and treated by the chromate method for the preparation of pure yttria.

In using this method for fractional separation, the ignited oxides were mixed dry with the calculated amount of chromic acid by shaking in an eight-liter, round bottom Jena flask, and then adding about 200 cc. of water. A violent reaction resulted, the dichromates being formed with the evolution of much heat. The whole was diluted to four liters and a ten per cent. solution of potassium chromate added until a permanent cloudiness resulted. The flask was then heated to boiling over a sand bath and, while vigorously stirred by passing a current of steam through the solution, a ten per cent. solution of potassium chromate was added drop by drop from a separatory funnel, various amounts being added according to the particular fraction desired. After all the chromate solution was added the boiling was continued for one or two hours, the current of steam and the flame under the sand bath being so adjusted as to maintain a constant volume.

After cooling sufficiently, the precipitate was filtered off and treated with concentrated hydrochloric acid in a casserole. When the first vigorous reaction was over the casserole was placed on a steam bath and a few cc. of alcohol or a few grams of sugar added to complete the reduction of the chromate. Unless the chromate is entirely reduced before adding

[1] THIS JOURNAL, 30, 182, 979 (1908).
[2] Ber., 33, 42 (1900).

oxalic acid, it is reduced to such a form as to be very difficult to separate from the rare earth oxalates by washing.

The bright green solution was diluted and the rare earths precipitated from the hot solution by hot oxalic acid solution. If properly carried out, all chromium may be removed by this method, but not all the potassium. This process was repeated until no more fractions were obtained. By this method various yttrium materials were fractionated as indicated below:

I. Xenotime earth, being a mixture of the middle fractions of a former chromate fractionation and having an average atomic weight of 94.0. 175 grams of oxide were mixed with the required quantity of chromic acid to form the dichromates, diluted to four liters and fractionated, 500 cc. of ten per cent. potassium chromate solution being used to each fraction.

II. Xenotime earth (average at. wt. 98.6), mixture of the first fractions from the same source as No. 1. 145 grams of oxide were taken.

III. Xenotime earth (average at. wt. 133.6), *yttrium-holmium* fractions from a bromate series. Oxalate white, but oxide light brown. Two 175 gram portions were taken and each was mixed with 370 grams of chromic acid. 500 cc. chromate solution were used in each fraction.

IV. Yttrium-erbium earth (average at. wt. 92.5) from the bromate fractionation. A 265 gram sample was mixed with twice its weight of chromic acid and divided into two flasks for the run. 500 cc. of the chromate solution were used for each fraction.

V. Xenotime earth (average at. wt. 96.2), last fraction from the same source as Nos. I and II. Slight spectra, color almost white. 190 grams of the oxide were mixed with 380 grams of chromic acid and fractionated in two flasks.

VI. Two hundred and eighty-eight grams of oxide (average at. wt. 92.3), obtained from colorless fractions of the bromate series were mixed with 725 grams of chromic acid and divided between two flasks. 500 cc. of ten per cent. chromate solution were added for each fraction except No. 2, which was obtained by evaporating solutions down to volume.

VII. The source of material was the same as for No. VI, but the process was carried out according to a method suggested by Professor C. James in a private communication. 144 grams of oxide were dissolved in nitric acid to a neutral solution and some potassium dichromate added, the solution diluted to four liters and fractionated with 500 cc. of chromate solution as above.

VIII. The following fractions from the above series were combined:

| Fraction. | Weight. Grams. | Atomic weight. |
|---|---|---|
| $III_{10}$ | 6 | 90.6 |
| $IV_5$ | 21 | 90.4 |
| $IV_6$ | .26 | 90.2 |
| $IV_7$ | 21 | 90.0 |
| $V_4$ | 75 | 90.0 |
| | 149 | 90.2 (calculated) |
| | | 90.3 (det'd) |

The combined oxide was mixed with 390 grams of chromic acid and 250 cc. of 10% chromate solution for each fraction except the last four, in which 500 cc. were used.

IX. Gadolinite earth (average at. wt. 91.2). 46 grams of a pure white oxide, which had been obtained from bromate fractions of gadolinite material and which had also been fractionated by the magnesium oxide and the potassium double sulfate methods, were mixed with 165 grams of chromic acid and fractionated by the use of 250 cc. of chromate solution per fraction.

A *yttrium-didymium* earth was also tried, but no successful separation was attained. Although the didymium did concentrate somewhat in the first fractions, yet it remained in considerable quantities until the end, so it was concluded that pure yttria cannot be prepared from material containing didymium by this method unless the didymium is first removed by saturation with potassium sulfate.

The results of the fractionations are shown in Table I. The series are arranged horizontally, the upper numbers in each case being the atomic weights of the fractions, and the lower numbers being the grams per fraction. From these results it may be concluded that the method serves very well for the preparation of fairly pure yttria.

### Determination of the Equivalent Weight.

The method used in the determination of the atomic weights was the conversion of weighed quantities of oxide to anhydrous sulfate. Since yttrium has no visible absorption spectra the atomic weights were depended on to show both the course of the fractionation and the purity of the material in the final fractions. However, there seemed to be considerable uncertainty about the results by this method, for if not heated enough to thoroughly dehydrate and remove the excess of acid the results would be low, and if heated too much a basic sulfate was formed and the results would be high. So it was evident that by varying the heating process of the sulfate almost any atomic weight value within certain limits could be obtained. Even where run in pairs, each sample undergoing identically the same treatments, good checks were not always secured.

OBSERVATIONS ON THE RARE EARTHS.

## TABLE I.—CHROMATE FRACTIONS.

| Fraction. | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. | 11. | 12. | 13. | 14. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | 94.0 | 95.4 | 97.4 | 102.2 | 95.9 | 93.8 | 92.9 | 91.6 | 90.4 | 89.8 | 89.8 | 89.8 | 89.8 | |
| | 175.0 | 2.0 | 7.0 | 31.0 | 20.0 | 22.0 | 20.0 | 14.0 | 16.0 | 15.0 | 12.0 | 4.0 | 3.0 | |
| II | 98.6 | 109.5 | 108.2 | 111.1 | 98.6 | 95.2 | 92.5 | 90.9 | 90.7 | 90.3 | | | | |
| | 145.0 | 5.0 | 28.0 | 20.0 | 21.0 | 20.0 | 15.0 | 14.0 | 9.0 | 5.0 | | | | |
| III | 123.6 | 144.9 | 145.0 | 139.9 | 137.6 | 128.3 | 110.2 | 101.8 | 93.6 | 93.4 | 90.6 | | | |
| | 350.0 | 9.0 | 87.0 | 48.0 | 46.0 | 30.0 | 38.0 | 32.0 | 17.0 | 17.0 | 16.0 | | | |
| IV | 92.5 | 94.9 | 94.5 | 92.8 | 93.0 | 90.4 | 90.2 | 90.0 | 89.5 | | | | | |
| | 265.0 | 20.0 | 54.0 | 40.0 | 40.0 | 21.0 | 26.0 | 21.0 | 35.0 | | | | | |
| V | 93.0 | 96.2 | 93.6 | 92.5 | 90.2 | | | | | | | | | |
| | 190.0 | 50.0 | 37.0 | 29.0 | 75.0 | | | | | | | | | |
| VI | 92.3 | 93.8 | 92.9 | 91.5 | 90.8 | 90.4 | 89.9 | 89.8 | 89.2 | | | | | |
| | 288.0 | 48.0 | 12.0 | 40.0 | 33.0 | 45.0 | 43.0 | 35.0 | 28.0 | | | | | |
| VII | 92.3 | 96.0 | 93.2 | 92.2 | 91.5 | 91.4 | 90.9 | 90.2 | 89.2 | | | | | |
| | 144.0 | 6.0 | 12.0 | 9.0 | 24.0 | 12.0 | 12.0 | 15.0 | 51.0 | | | | | |
| VIII | 90.3 | 95.1 | 94.6 | 93.1 | 90.7 | 91.1 | 90.9 | 90.3 | 90.7 | 90.3 | 90.1 | 90.0 | 89.7 | 89.5 89.7 |
| | 149.0 | 6.0 | 9.0 | 9.0 | 5.0 | 12.0 | 10.0 | 9.0 | 8.0 | 9.0 | 3.0 | 17.0 | 15.0 | 19.0 12.0 |
| IX | 91.2 | 93.0 | 91.7 | 90.7 | 91.2 | 90.1 | 89.1 | | | | | | | |
| | 47.0 | 2.0 | 11.0 | 5.0 | 10.0 | 6.0 | 5.0 | | | | | | | |

Upper row of each series is average atomic weight of fractions.
Lower row is grams of oxide in each fraction.

Since it was evident that no exact knowledge of the purity of the oxide could be obtained by this method, the further fractionation of the material was considered impractical until a reliable method was found for the determination of the atomic weights.

Three lines of procedure suggested themselves: 1st, to study conditions and endeavor to obtain more consistent results from the $Y_2O_3$ : $Y_2(SO_4)_3$ ratio, and to compare it with other methods; 2nd, to prepare anhydrous yttrium chloride and find the ratio $YCl_3$ : 3Ag, as Baxter and Chapin[1] have already done for neodymium; and, 3rd, to determin the ratio $Y_2O_3$ : $2YCl_3$. With this purpose in view the fractions containing the best material ($VIII_{11}$, $VIII_{12}$, $VIII_{13}$, $VIII_{14}$, $VI_8$ and $VII_8$) were combined and purified as follows:

The oxide was dissolved in pure hydrochloric acid and precipitated as oxalate with pure oxalic acid and washed until all traces of chromium were removed. After ignition in platinum dishes in an electric oven the oxide was again dissolved in hydrochloric acid and a portion of the solution treated with hydrogen sulfide. No precipitate was formed, so the solution was diluted considerably and saturated with potassium sulfate, an excess of the solid being added. After standing a week only a slight cloudiness had developed and the solution was filtered until perfectly clear and ammonia water added in excess. After digesting on the steam bath for an hour with the occasional addition of more ammonia to prevent the solution of the hydroxide, it was washed until all but traces of the alkali or alkaline earths were removed. The hydroxide was dissolved in pure acid and reprecipitated as oxalate, thoroughly washed dried and ignited in platinum dishes as before. The oxide was again redissolved and reprecipitated, especial care being taken to exclude dust. This precipitation was done with recrystallized oxalic acid, then the precipitate was thoroughly washed and ignited in the electric oven at as low a temperature as possible to prevent possible contamination from the platinum dishes. The earth was now considered to be free from the common metals.

### Ratio of Oxide to Sulfate.

It seemed probable that if a set of conditions were selected which would give the most probable value for the atomic weight and these conditions were followed in each case a set of relative values would be obtained which would demonstrate the course of a fractionation, even if not giving absolute results.

Wild[2] states that all traces of acid were not expelled until a temperture of 450–500° was reached.

The following procedure was tried: Small samples (generally 0.2 to

[1] THIS JOURNAL, 33, 17 (1911).
[2] Z. anorg. Chem., 38, 196 (1904).

0.5 g. oxide) were weighed in platinum crucibles. The oxide was then carefully moistened with water, and covered with pure hydrochloric acid, placed over a steam bath, and protected from dust. When dissolved, a slight excess of the calculated amount of dilute sulfuric acid was added and the solution evaporated to dryness. It was then heated for four hours in an electric furnace at 500°, and weighed. To prevent absorption of moisture from air by the anhydrous sulfate, the crucibles were placed in weighing bottles while still hot and weighed when cold, first loosening the covers for an instant to allow the air pressure to equalize. All weighings were made by the method of substitution, the tare being a platinum crucible of same size and shape as the others and enclosed in a similar weighing bottle. The tare crucible was also placed in the furnace during the heating and in all respects was subjected to the same treatment as the crucibles containing the samples. The sulfates were finally treated with water to determin if basic sulfate had been formed. The temperature of Nos. 9 and 10 was held at 400° to 425° instead of 500°. The ratio used in calculating the atomic weights was:

$$\frac{M + 24}{M + 144.105} = \frac{\text{wt. of oxide}}{\text{wt. of sulfate}}$$

where M is the atomic weight desired. All weights were corrected to vacuum. The results obtained by this method are given in Table II. It will be noted that the concordance obtained was far from satisfactory.

TABLE II.

| No | $O = 16$ Weight of oxide. | $Y_2O_3 : Y_2(SO_4)_3$ Weight of sulfate. | Atomic weight. | $S = 32.07$ Solubility of the sulfate in water. |
|---|---|---|---|---|
| 1 | 1.00552 | 2.06854 | 89.61 | |
| 2 | 0.87756 | 1.79829 | 88.96 | |
| 3 | 0.20640 | 0.42557 | 89.11 | |
| 4 | 0.19823 | 0.40993 | 88.46 | |
| 5 | 0.26409 | 0.54237 | 89.97 | (Partially insoluble) |
| 6 | 0.36243 | 0.74383 | 90.13 | |
| 7 | 0.34745 | 0.71295 | 90.17 | (Partially insoluble) |
| 8 | 0.28690 | 0.58787 | 90.52 | |
| 9 | 0.22910 | 0.47098 | 89.76 | (Small, insoluble residue) |
| 10 | 0.27464 | 0.56434 | 89.86 | |
| 11 | 0.18760 | 0.38580 | 89.68 | (Small, insoluble reisdue) |

## Preparation of Yttrium Chloride.

The oxide was dissolved in 20% hydrochloric acid which had been redistilled through Jena glass of good quality, the middle fractions only being taken. The solution was filtered and evaporated until the salt crystallized on cooling. This was then crystallized several times from conductivity water, the mother liquor in each case being drained off thoroughly by means of a centrifugal machine. The chloride was pure

white and formed in small brilliant crystals. These were powdered in an agate mortar and kept in a vacuum desiccator over concentrated sulfuric acid. According to Matignon,[1] the salt crystallizes with six molecules of water and fuses at 160°, but loses five molecules of its water of hydration at 110°.

*Dehydration of the Yttrium Chloride.*—Matignon[1] prepared the anhydrous chloride by heating the hydrate in a current of dry hydrochloric acid gas at 180°. He describes the anhydrous chloride as fusing at about 686° and gives the density at 18°/4° as 2.8.

The method used for drying the chloride was based on Matignon's method and was carried out practically the same as the process described by Baxter and Chapin[2] in the preparation of anhydrous neodymium chloride.

Hydrochloric acid gas was generated by the action of concentrated sulfuric acid on concentrated hydrochloric acid and was dried by passage through two towers about one meter high and 2.5 cm. in diameter filled with glass beads over which trickled concentrated sulfuric acid.

Nitrogen was prepared by passing air through concentrated ammonia and then over hot copper slugs in a quartz tube. It was purified and dried by passing through dilute sulfuric acid, silver nitrate solution, concentrated sulfuric acid, and over solid potassium hydroxide, and then through a tower similar to those described above but only one-half meter high, and finally through a phosphorus pentoxide tube. Air was purified and dried in a similar train, omitting the ammonia and copper treatments. The apparatus for drying the gases was composed entirely. of glass and was so arranged that either hydrogen chloride, nitrogen, air or a mixture of hydrogen chloride and nitrogen could be passed through the apparatus as desired.

In the first experiments the chloride to be dehydrated was contained in a quartz boat which had previously been weighed in a weighing bottle. The boat and contents were then heated in a Jena glass tube which formed part of a "Richards bottling apparatus." However, it was found that the chloride could not be heated to a sufficiently high temperature in this apparatus to insure perfect dehydration because of the softening of the glass tube and the danger of contamination through action of the acid fumes on the alkali in the glass at this temperature.

In the later experiments the bottling apparatus and boat were replaced by a "quartz reaction flask" (Fig. 1) which was originally designed for work being done in this laboratory on the atomic weight of tantalum.

About five grams of the hydrate were placed in the weighed flask, which was then attached to the gas trains. A small asbestos oven was

[1] *Compt. rend.*, **134**, 1308 (1902); *Ann. chim. phys.*, [8] **8**, 439 (1906).

[2] THIS JOURNAL, **33**, 17 (1911).

set up around the bulb. After displacing all the air with nitrogen the temperature was raised to 110°–120° and a mixture of dry nitrogen and dry hydrogen chloride was passed through the flask. Most of the water was driven off at this temperature. When water had ceased to come off, the temperature was slowly raised to 200°, then pure dry hydrogen chloride alone was passed through the flask and the temperature raised to 360° and held for one hour. The oven was then removed and the chloride fused with the flame of a Bunsen burner applied directly to the quartz
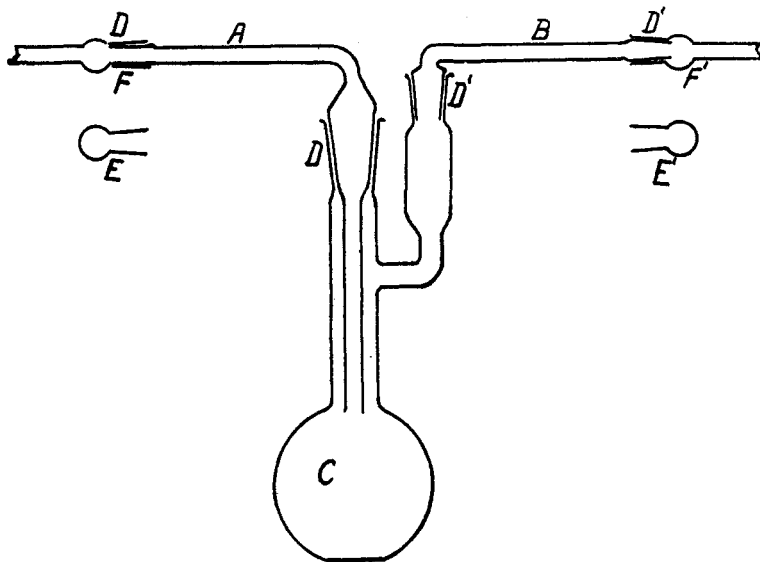


A, B and C are fused transparent silica. D, D, D′, D′, carefully ground joints.
Caps E, E′, and tubes F, F′, are made of soft apparatus glass.

bulb. If fused at a dull hed heat to a clear, quiet liquid, that did not wet the quartz but formed globules which on solidifying loosened from the flask and dissolved to a perfectly clear solution in water. The chloride was allowed to cool in a stream of pure hydrogen chloride. This was displaced by nitrogen and that in turn by air. In order not to admit any moist air to the flask the outlet tube F′ was removed and the cap E′ adjusted while the dry air was still passing. This caused a slightly increased pressure inside the flask and when the inlet tube F was removed and the cap E quickly substituted the dry air moved back and prevented any moisture entering the flask. The flask was then transferred to the balance and weighed.

*Ratio of Yttrium Chloride to Silver.* — All attempts to determin this ratio have been as yet unsuccessful for reasons not fully understood. Several trials were made by dissolving a weighed sample of anhydrous chloride (usually about 3–4 grams) prepared by the method described

above, in one liter of water and adding to this solution a silver nitrate solution prepared as follows:

A quantity of pure silver equivalent to the yttrium chloride to within a very few tenths of a milligram (assuming the at. wt. $Y = 89$) was weighed out and dissolved in pure nitric acid (sp. gr. $1.2$) which had been redistilled from quartz apparatus. Enough acid was added so that an excess remained. The reaction was carried out in a $1.5$ liter (Jena) Erlenmeyer flask fitted with a column of bulbs to retain spray. When the silver was entirely dissolved some water was added and the solution gently boiled to remove nitrogen oxide fumes. It was then diluted to one liter and added very slowly to the chloride solution. The flask was stoppered and contents well shaken with a rotary motion, and allowed to stand a few days. Small samples were then removed and tested for an excess of silver or chloride ion. In every case the silver ion was found in large excess, although the solution was allowed to stand in a dark place for a week, and in some cases it was heated on the steam bath for several hours to bring about complete equilibrium.

Another determination was attempted assuming the atomic weight of the material to be 90, but in this case also considerable excess of silver ion was found. These results were evidently caused by one of three possibilities:

1. Adsorption of the molecular yttrium chloride by the silver chloride. This seemed improbable since rather dilute solutions were used and the silver nitrate solution was added very slowly to the yttrium chloride solution, also the fact that the solution was allowed to stand long enough for most of the occluded yttrium chloride to come back into solution.

2. That yttrium chloride may not be completely ionized under these conditions. Lack of time has prevented the confirmation or disproval of this possibility in the present investigation.

3. The atomic weight of the metal was above 90. The value 89 had been assumed to be close to the true value from inspection of the results from the $Y_2O_3 : Y_2(SO_4)_3$ ratio (Table II). However, since these results were very unsatisfactory, this was thought to be the most probable cause of the discrepancies and this work was temporarily abandoned until more reliable atomic weight values for the material were obtained by another method.

### Ratio of Yttrium Oxide to Yttrium Chloride.

This ratio seemed desirable because, unlike the sulfate method, both substances involved could be prepared with definit composition and weighed as such. Therefore, atomic weight values with an accuracy of 2 in the second decimal place (assuming an analytical error of $0.001\%$) ought to be obtained, and these values would serve as a starting value in the chloride-silver ratio.

In order to obtain this ratio it was decided to convert a weighed quantity of yttrium oxide to anhydrous chloride and determin its weight. About 0.7–1.0 gram of pure oxide contained in a platinum dish was heated for eight to ten hours at a bright red heat in an electric furnace. This was done to insure complete decomposition of any carbonate present. The oxide, while still hot, was poured into the quartz reaction flask, which had been previously weighed. This was easily done by means of a dry glass funnel with large caliber stem reaching to the bottom of the flask.

The flask was placed in a desiccator over concentrated sulfuric acid until cold, then the caps were adjusted and the flask was hung in the balance until equilibrium was reached and then weighed.

The oxide was carefully moistened and finally covered with conductivity water and the flask attached to the gas apparatus and pure hydrogen chloride passed in until the oxide was entirely dissolved. The oven was adjusted about the bulb, and while the temperature was kept at 100° dry air was passed through the flask until the chloride was dry. Under these conditions of evaporating to dryness from strong hydrochloric acid solution the chloride remains as a compact, hard mass on the bottom of the flask. It was found best to redissolve by adding a little conductivity water and again evaporating to dryness from a nearly neutral solution. This gives the chloride in a crystallin form and apparently less dense, since it is more voluminous and dehydration in more easily and smoothly accomplished.

The air was displaced by a dry nitrogen and hydrogen chloride mixture and the temperature raised to 120° and held until water of hydration ceased to be evolved. Five of the six molecules of water present come off at this temperature. The temperature was then allowed to slowly rise to 200° and after some time dry hydrogen chloride alone was passed through the apparatus and the temperature raised to 360° and maintained at this point for one and one-half hours. Care was taken to dehydrate entirely by efflorescence, for if the salt was allowed to fuse before it was entirely dehydrated, basic chloride was formed, which not only gave high results but also attacked the quartz flask, when the final fusion was made.

Care was also taken to avoid loss by volatilization during fusion. This was done by protecting the upper part of the flask from heat by means of an asbestos shield and by stopping the current of hydrogen chloride just before fusion, so that while the fusion was carried out in an atmosphere of hydrogen chloride still there was no current to sweep out vapors of yttrium chloride before they could condense in the cooler parts of the flask. No. 3, in Table III, was made without this precaution, while Nos. 4, 5 and 6 were safeguarded against volatilization. As soon as the fusion was complete the mass was allowed to solidify and the gas current

again started while the temperature of the flask was still about 400 to 500° in order to remove any water vapor expelled during fusion. When cool, the hydrogen chloride was replaced by nitrogen and this in turn by dry air. The flask was removed and weighed as described in the preparation of anhydrous yttrium chloride.

Six determinations were made, Nos. 1 and 2 were lost because of imperfect dehydration before fusion, with the result that considerable basic chloride was formed. No. 3 is included in the table, although the result is high. This was due to the fact that the precautions to prevent volatilization were not taken. All weights were made by the method of substitution. The tare flask was a quartz flask as nearly as possible like the one used in the reactions. All weights were corrected to vacuum. The specific gravity of the oxide was taken as 5.046 (Nilson and Pettersson[1]) and that of the chloride as 2.8 (Matignon). The ratio used in calculation of the atomic weights was:

$$\frac{M + 24}{M + 106.38} = \frac{\text{Weight of oxide}}{\text{Weight of chloride}}.$$

### TABLE III.

| $O = 16$ | | $Y_2O_3 : 2YCl_3$ | $Cl = 35.46$ |
|---|---|---|---|
| No. | Weight of oxide. | Weight of chloride. | Atomic weight. |
| 3 | 0.72180 | 1.24092 | 90.54] |
| 4 | 0.80392 | 1.38437 | 90.10 |
| 5 | 0.70050 | 1.20610 | 90.14 |
| 6 | 0.73030 | 1.25755 | 90.11 |

## Summary.

Rare earth mixtures from gadolinite and xenotime were fractionated by various methods. The efficiency of the chromate method, as applied to various fractions from the bromate method, was studied. It was found to be a rather rapid method for the preparation of small quantities of good yttria from mixtures containing erbium, holmium, etc., in small amounts, but not suited to fractionation of earth mixtures containing didymium or gadolinium unless these are first removed by the potassium sulfate method.

The determination of the ratio $Y_2O_3 : Y_2(SO_4)_3$ as a means of finding the atomic weight of yttrium was studied and found to be rather uncertain. The method apparently gives atomic weight values which are lower than those gained by other, more reliable methods.

The ratio $Y_2O_3 : 2YCl_3$ was studied and some very consistent results were obtained. Weighed quantities of yttrium oxide were converted to anhydrous yttrium chloride in a quartz flask, and weighed. Three values varying between 90.10 and 90.14 were obtained. By a more careful study of the details this variation can probably be reduced by half.

[1] Ber., 13, 1459 (1880); Compt. rend., 91, 232.

Yttrium material was prepared having only a very faint spectra in 10 cm. layers of saturated solutions of the chloride. It was considered to have not more than one-half per cent. erbium present. The average atomic weight obtained by the oxide-chloride method was 90.12.

This work is being continued, with the hope of preparing pure yttrium oxide for the final determination of the atomic weight of yttrium. It may be well to mention that similar work is under way with samarium and gadolinium.

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# AN ESTER OF HYDROCOBALTICYANIC ACID.

By C. E. Bolser and L. B. Richardson.

While hydrocobalticyanic acid, which was discovered by Zwenger[1] in 1847, and many of its metallic salts are substances more or less familiar to chemists, we have been unable to find references to the formation of esters of the acid. It occurred to us that it might be possible to synthesize some of these substances, and that their conduct might afford information as to the structure of this class of compounds. We have been successful in producing but one of them, the ethyl compound; and that probably not in a state of absolute purity; but the reactions which it may be made to undergo are of some interest in the study of the general nature of the class of substances to which hydrocobalticyanic acid, hydroferricyanic acid, etc., belong.

The general method used for the preparation of the ethyl ester was the usual treatment of the silver salt of the acid, suspended in alcohol, with ethyl iodide. Inasmuch as the acid is rather unstable at high temperatures, the reaction was carried on at the boiling point of the mixture. No decomposition seemed to take place under these circumstances, and the gradual yellowing of the suspended solid, indicating the formation of silver iodide, showed that the desired reaction was taking place. The exact course of procedure was as follows:

Twenty grams of potassium cobalticyanide were precipitated by silver nitrate in excess, and the silver cobalticyanide, washed with very dilute nitric acid, then with water, and finally with alcohol, was placed in a liter flask. The flask was fitted with a return condenser. 250 cc. of 95% alcohol were added, and the mixture was heated to the boiling point. An amount of ethyl iodide slightly in excess of the theoretical quantity was then poured in, and the boiling continued for an hour. The hot mixture was filtered rapidly, and the filtrate evaporated at once under reduced pressure (40 mm.). It is most important that this evaporation take place immediately; otherwise the iodine produced by the decomposition of the excess of ethyl iodide contaminates the products, and can be removed from

[1] Ann., 62, 157.