consists of a saturated solution of carbonic acid under the partial pressure of the carbon dioxide in the atmosphere, and contains no other conducting impurities in appreciable quantity.

In a following paper some practical applications of this result in the correction of conductivity determinations at high dilutions will be developed, and further evidence of its validity will be brought forward.

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[Contribution from the Chemical Laboratories of New Hampshire College.]

THE RARE EARTH COBALTICYANIDE.

By C. James and P. S. Willand.

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The first rare earth cobalticyanide was prepared by Cleve and Hoeglund.[1] In 1915 the cobalticyanides were examined during a search for a method to separate yttrium from erbium,[2] and owing to the facts that the separation of yttrium from erbium was rapid, and that neodymium collected in the most soluble fractions, further investigations were carried out with the following results:

Neodymium Cobalticyanide, $Nd_2(CoC_6N_6)_2.9H_2O$.—This compound was easily precipitated from a boiling solution of neodymium chloride by adding potassium cobalticyanide. Neodymium chloride was kept in excess. The salt, which possessed a pale lilac color, formed a heavy crystalline powder. Microscopic examination showed that the crystals belong to the hexagonal system. They were almost insoluble in water, very slightly soluble in concentrated hydrochloric acid, and rapidly decomposed by boiling sodium hydroxide.

In order to determine the percentage of neodymium, some of the material was boiled with sodium hydroxide to decompose it. The hydroxide, after filtering and washing well, was dissolved in dilute hydrochloric acid and precipitated as the oxalate. This was ignited and weighed. The average for the neodymium amounted to 32.80 per cent., which seemed to indicate that the formula should be $Nd_2(CoC_6N_6)_2.9H_2O$. The cobalt was determined by electrolysis after breaking up the salt by fusion with bisulfate and rendering the solution alkaline by ammonium hydroxide. The results were a little below the theoretical.

When the compound was heated it gave off water and gradually turned blue. At higher temperatures it underwent rapid decomposition with the evolution of sparks.

Yttrium Cobalticyanide, $Y_2(CoC_6N_6)_2.9H_2O$.—This salt was prepared by precipitating a boiling solution of yttrium nitrate with a hot solution of potassium cobalticyanide.

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[1] *Bull. soc. chim.*, — 193–201 (1873).

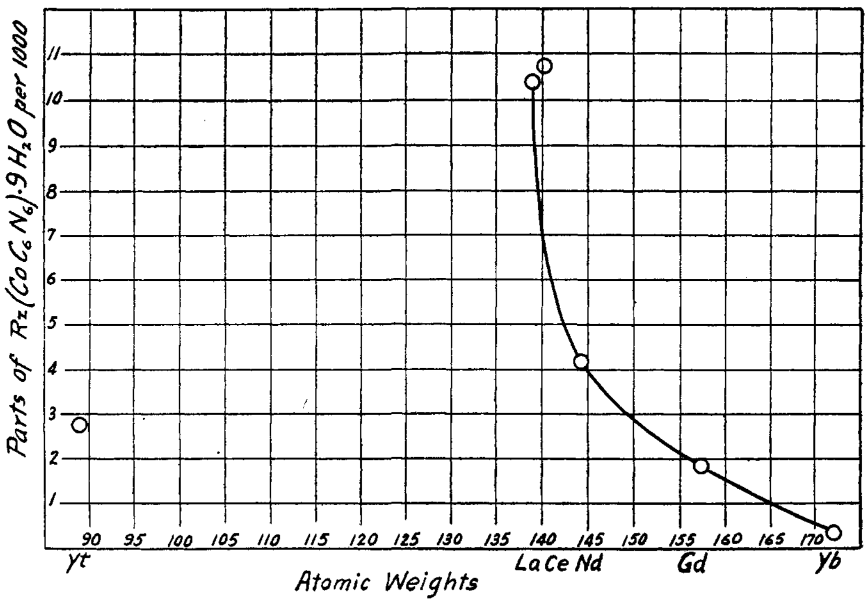
[2] This Journal, 37, 2642 (1915).

The precipitate was crystalline and creamy white in color. It was almost insoluble in water and hydrochloric acid, but was decomposed by boiling with sodium hydroxide.

The percentage of yttrium was determined in a similar manner to that of neodymium. The yttrium found amounted to 22.95%, indicating the presence of nine molecules of water of crystallization. From this it would seem that the rare earth cobalticyanides possess the type formula $R_2(CoC_6N_6)_2.9H_2O$.

Other cobalticyanides were prepared in a similar manner to those described above. The lanthanum salt formed a heavy precipitate consisting of hexagonal bipyramids. They were a little more soluble in water than the neodymium compound, and were somewhat soluble in concentrated hydrochloric acid. Cerium cobalticyanide was obtained as a white crystalline precipitate with a slightly yellow tint. The solubility in water and concentrated hydrochloric acid was of about the same degree as the lanthanum salt. Gadolinium cobalticyanide formed very quickly. The precipitate was very finely divided and almost insoluble. Ytterbium cobalticyanide was white, crystalline and insoluble. When a solution of potassium cobalticyanide was boiled with a solution of thorium nitrate, no precipitate formed, even though the original volume had been greatly reduced.

In order to obtain some comparison of the solubilities of these compounds, they were rotated in a thermostat with 10% hydrochloric acid. Three grams of each salt were placed in a bottle with 50 cc. of hydrochloric



acid having a sp. gr. of 1.050 at 15°. After they had rotated for two weeks at 25°, they were allowed to settle. Some of the liquid was weighed, precipitated with oxalic acid and allowed to stand fifteen hours before filtering, igniting and weighing. From these results the parts per thousand were calculated and plotted against the atomic weights.

Compound.	Atomic weight.	Parts per thousand.
$La_2(CoC_6N_6)_2.9H_2O$	139.0	10.41
$Ce_2(CoC_6N_6)_2.9H_2O$	140.25	10.75
$Nd_2(CoC_6N_6)_2.9H_2O$	144.3	4.19
$Gd_2(CoC_6N_6)_2.9H_2O$	157.3	1.86
$Yb_2(CoC_6N_6)_2.9H_2O$	172.0	0.38
$Y_2(CoC_6N_6)_2.9H_2O$	89.0	2.78

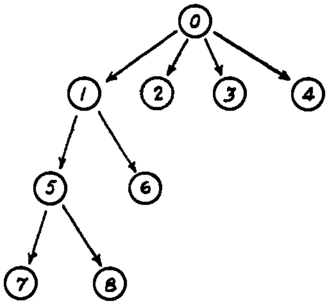
The curve obtained from the above data shows that yttrium cobalticyanide is of about the same solubility as the samarium and europium compounds, and more than three times more soluble than the erbium salt. The separation of yttrium and terbium would seem to be less efficient, since the terbium salt is about twice as soluble as that of erbium.

Separation of Mixed Oxides.

1. Oxides containing dysprosium, holmium, and yttrium, with traces of erbium, terbium and neodymium. These were dissolved in nitric acid, diluted to about 600 cc., boiled, and a solution of potassium cobalticyanide added until a quantity of precipitate had formed. This was filtered off and the process repeated. The precipitates were boiled with sodium hydroxide, filtered, washed and dissolved in nitric acid. The solutions were then precipitated as the oxalates, ignited and again converted into the nitrates, the solutions of which were examined by means of a spectroscope.

Fraction I showed very strong holmium and dysprosium bands and traces of neodymium and erbium. In Fraction II holmium and dysprosium were still very strong, neodymium was weak and there was a trace of erbium. Fraction III showed strong neodymium dysprosium and holmium bands. There was a slight trace of erbium. In Fraction IV, neodymium was stronger while holmium and dysprosium were weak. The material was mainly yttrium nitrate.

Fraction I was diluted, boiled and more cobalticyanide added. The precipitate that formed was filtered off and the remaining rare earth thrown out as the oxalate. These Fractions, V and VI, were converted to the oxides. V was again dissolved in nitric acid and split into two more fractions as shown in the sketch herewith.



In color the oxides varied from a chocolate-brown to a light chamois proportional to the equivalents, showing that terbium tends to go to the least soluble end. All the oxides were boiled with water to remove any alkali metal before the equivalents were determined.

No. of fraction.	II.	III.	IV.	VI.	VII.	VIII.
Atomic weight.......	109.5	95.2	89.0	102.3	132.9	122.4

2. Separation of erbium from yttrium. The oxide used was very rich in erbium. Twenty-five grams were dissolved in hydrochloric acid, diluted to about 800 cc. and precipitated as in the case of the dysprosium, holmium and yttrium oxides. Two fractions were taken, and these, after converting to oxides and redissolving, were again fractioned. Fraction I gave Fractions III, IV and V, while Fraction II gave Fractions VI and VII. The oxides varied from a rose color to an extremely pale pink. Fraction III, the least soluble, possessed the most color, and Fraction VII, the most soluble, was the palest.

No. of fraction.	III.	IV.	V.	VI.	VII.
Atomic weight...........	142.3	137.2	127.8	110.1	93.7

The cobalticyanide method is excellent for the separation of yttrium from erbium and *vice versa*. The precipitates are very crystalline, and the process can be quickly carried out.

One of the authors and another are investigating the ferricyanides, which are nice crystalline compounds and which differ very considerably in their solubilities. By fractionally precipitating a solution of the nitrates of yttrium and erbium with potassium ferricyanide, a rapid separation is effected.

DURHAM, N. H.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY, NO. 271.]

AMMONIUM IODIDE, ITS SOLUBILITIES AND THE ABSENCE OF A TRANSITION POINT.

BY ALEXANDER SMITH AND HERBERT E. EASTLACK.

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Wallace[1] observed no irregularities in the cooling curves of ammonium iodide between 220° and —16.5°, and no change under the microscope between 16° and the sublimation point. He notes that, while the chloride and bromide crystallize in pentagonal icositetrahedra, there is some evidence that above their transition point they are cubical, just like the iodide, and the alkali iodides. He refers also to Tuton's[2] statement that the molecular volumes of ammonium sulfate and its double salts lie between those of rubidium and caesium, and himself found that, of the am-

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[1] *Centr. Min.*, 1900, 33.

[2] *Z. Kryst.*, 38, 602 (1904); 41, 321 (1906).