

containing the acid was buried in an ice-bath and the temperature of the liquid noted by a thermometer inserted through a rubber stopper. The apparatus was air-tight. A stream of hydrogen gas was continued through the apparatus in one experiment for six weeks and in another two months. On two occasions when the ice in the bath had melted in going over Sunday, the temperature rose to 10° C. The temperature could not possibly have remained that high for over twelve hours, which would have had small influence when the experiments lasted through a number of days. The temperature was reported 0° - 10° C., however. Not only copper sulphate, but cuprous sulphide and sulphur dioxide had also formed. Copper, therefore, decomposes concentrated sulphuric acid (sp. gr. 1.84) practically at zero.

From my own experiments and from experiments performed with apparatus similar to that used by Andrews and under the same conditions, except with regard to the important element, time, which consideration is necessary for all chemical reactions, the author must adhere to his former statement.

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THE SEPARATION OF THORIUM FROM THE OTHER RARE EARTHS BY MEANS OF POTASSIUM TRINITRIDE.

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SOME time ago the author and F. L. Kortright¹ briefly described the action of a solution of potassium trinitride upon a neutral solution of the rare earths. It was found at that time that the flocculent precipitate which is produced was most probably thorium hydroxide, but our supply of potassium trinitride having been exhausted it was impossible to further investigate the reaction or ascertain the completeness of the separation. The immediate continuation of the work was prevented by unexpected difficulties which were encountered in the preparation of pure hydronitric acid on a large scale. These difficulties have since been removed, and it has been possible to prepare an amount of the reagent sufficient for the investigation described below.

¹ *Ztschr. anorg. Chem.*, 6, 35; *Am. Chem. J.*, 16, 79.

The solution of potassium trinitride which was used was prepared by carefully neutralizing a dilute solution of hydronitric acid with a dilute solution of pure caustic potash and then adding hydronitric acid sufficient to give to the solution a distinctly acid reaction. The solution first employed contained about three and two-tenths grams of potassium trinitride to the liter.

Before studying the separation of thorium from the other rare earths, the reaction between potassium trinitride and pure thorium chloride was first investigated. The thorium employed was from a sample of thorium oxalate, which had been very kindly presented to me by Dr. Theodor Schuchardt, of Goerlitz. It was found to be of a very high grade of purity, but to guard against the possible presence of other rare earths, the oxalate was converted to the oxide by ignition, treated with concentrated sulphuric acid, the anhydrous sulphate dissolved in distilled water at a temperature of 0° , and this solution was precipitated with pure oxalic acid. The precipitated thorium oxalate was thoroughly washed with hot water containing one per cent. hydrochloric acid, and was then dropped into a hot, concentrated solution of ammonium oxalate. It dissolved completely and no precipitate formed when the solution was diluted and cooled. From this solution the thorium was again precipitated as oxalate by means of strong hydrochloric acid and was then brought into solution as thorium sulphate in the manner described above. It was then precipitated by ammonium hydroxide and the precipitate thoroughly washed with water. The thorium hydroxide was then dissolved in hydrochloric acid, ammonium hydroxide was added until a faint but permanent precipitate remained, and this was then removed by filtration. There was thus obtained a neutral solution of thorium chloride containing a very small amount of ammonium chloride.

The strength of this solution of thorium chloride was ascertained by precipitating portions of ten cc. each with ammonium hydroxide, filtering, washing, igniting, and weighing as ThO_2 . Two determinations gave, for thorium oxide in ten cc., 0.0591 gram and 0.0595 gram. The mean of these results is equivalent to 0.00521 gram thorium in one cc.

Upon adding to this thorium solution a few cc. of the solution

of potassium trinitride, the precipitate which, in the previous work with Dr. Kortright, had formed at once, failed to appear; upon heating the solution to boiling, however, there was quickly formed a white, flocculent precipitate, closely resembling in appearance aluminum hydroxide, but settling rapidly when the flame was removed. In the first determinations the solution was boiled for five minutes, but it was later found that boiling for one minute is sufficient. During the boiling the odor of hydronitric acid was distinctly noticeable. The precipitate was washed by decantation with hot water, transferred to the filter, ignited, and weighed as ThO_2 . Twenty cc. of thorium chloride, containing, according to the determination with ammonium hydroxide, 0.1186 gram thorium dioxide gave, by precipitation with potassium trinitride, 0.1183 gram thorium dioxide, equivalent to 0.00520 gram thorium in one cc. instead of 0.00521 as obtained with ammonia.

It is apparent, therefore, that thorium can be quantitatively precipitated by potassium trinitride.

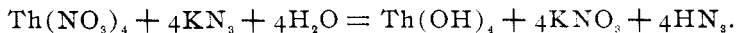
The previous work of Dr. Kortright showed that the thorium is probably precipitated as the hydroxide, but the tendency of the precipitate to absorb carbon dioxide rendered the analyses unsatisfactory. If, however, the thorium is precipitated as the hydroxide, then all of the hydronitric acid of the potassium salt first added must reappear in the filtrate from the thorium hydroxide and in the gas evolved during the boiling. To ascertain whether this took place the precipitation was made in a round bottomed flask. In the neck of the flask there was inserted a two hole rubber stopper, through one opening of which a current of purified air was admitted, the other opening carrying an upright condenser. The condenser was connected at the upper end with two absorption vessels containing neutral silver nitrate solution. As the hydronitric acid was to be determined by precipitation with silver nitrate, a neutral thorium nitrate solution, containing 0.0075 gram thorium in one cc., was substituted for the thorium chloride. The thorium nitrate solution was placed in the flask, potassium trinitride was added, and after starting a current of air through the apparatus, the contents of the flask was heated to boiling and kept boiling for two

minutes. Soon after the heating began a white precipitate of silver hydronitride formed in the first absorption flask containing the silver nitrate; by the time the reaction was complete this precipitate had become quite voluminous. The absorption of the gas by silver nitrate seems to be both rapid and complete, for nothing more than a slight opalescence ever appeared in the second absorption flask. After the apparatus had become cool the thorium hydroxide was filtered off and the filtrate was precipitated by silver nitrate. The silver trinitride thus obtained, together with that in the absorption flasks, was washed by decantation with cold water, the washings being passed through a hardened filter. When the wash water gave no further reaction for silver the funnel with the filter was placed in the neck of the flask containing the main part of the precipitate, and quite dilute, hot nitric acid was poured upon the paper. The silver trinitride on the paper dissolves almost immediately. After washing the paper with water, the funnel was removed and the contents of the flask was boiled until all of the silver trinitride had dissolved. The silver was then precipitated by hydrochloric acid and weighed as silver chloride. Ten cc. of thorium nitrate and ten cc. of potassium trinitride were used. The silver chloride resulting weighed 0.1447 gram, equivalent to 0.0434 gram hydronitric acid. The strength of the potassium hydronitride, which was a different solution from the one first employed, was then determined in the same manner.

5 cc. gave 0.0744 AgCl = 0.02232 HN₃,

5 cc. gave 0.0745 AgCl = 0.02235 HN₃.

Using the mean of these results, it appears that 0.0446 gram of hydronitric acid was used in the precipitation of the thorium nitrate, of which 0.0434 gram was recovered from the filtrate and distillate. That this latter result is somewhat low is doubtless due to the loss of hydronitric acid by volatilization during the filtration of the liquid in the flask. These results, together with those given in the preceding article already referred to, enable us to represent the reaction by the equation



This reaction is interesting not only because of the quantita-

tive precipitation of thorium by this means, but also because of the peculiar behavior of the potassium hydronitride. As Ostwald has stated, hydronitric acid is but slightly stronger than glacial acetic acid, and the above equation reminds one of the behavior of acetates towards ferric iron, the solution of ferric acetate being fairly stable in the cold, but breaking down upon heating, into acetic acid and ferric hydroxide.

The experiments detailed below were then made to ascertain whether thorium could be quantitatively separated from the other rare earths by means of the above reaction. A neutral solution of pure lanthanum chloride was first prepared and its strength determined by precipitating with ammonium hydroxide and weighing the lanthanum as La_2O_3 . The solution contained 0.00431 gram lanthanum in one cc. This solution gave no precipitate when boiled for some minutes with potassium trinitride. Fifteen cc. of this solution and fifteen cc. of the thorium chloride solution were placed in an Erlenmeyer flask, twenty-five cc. of potassium trinitride (three and two-tenths grams to the liter) was added and the solution was boiled for one minute. The precipitate was filtered off and washed with hot water, ignited, and weighed. To the filtrate five cc. more of potassium trinitride was added and the solution boiled for two minutes. No further precipitation resulted. The solution was then precipitated with ammonia and the lanthanum weighed as the oxide. The results were:

	Taken.	Found.
Thorium	0.0781	0.0777
Lanthanum	0.0646	0.0642

A mixture of the rare earths in Brazilian monazite was then freed from thorium by repeatedly digesting the mixed oxalates with a hot, concentrated solution of ammonium oxalate. The residual oxalates were then transformed into chlorides and dissolved in water. The solution showed the pink color and absorption bands of didymium and gave a strong reaction for cerium when treated with hydrogen peroxide and ammonia. When boiled with potassium trinitride it gave a very faint precipitate which was filtered off. By precipitation with ammonia this solution of cerium, lanthanum, didymium, etc., free from

thorium, was found to contain 0.0166 gram of the mixed oxides in one cc. The precipitation was made as in the separation from lanthanum and an excess of potassium trinitride was used in each case.

	Taken.	Found.
I. Thorium	0.1300	0.1294
Ce, La, Di oxides.....	0.0332
II. Thorium	0.0785	0.0783
Ce, La, Di oxides.....	0.0830
III. Thorium	0.0535	0.0526
Ce, La, Di oxides.....	0.2490
IV. Thorium	0.0535	0.0531
Ce, La, Di oxides.....	0.2490
V. Thorium	0.0550	0.0541
Ce, La, Di oxides.....	0.4980
VI. Thorium	0.0535	0.0550
Ce, La, Di oxides.....	0.5810
VII. Thorium	0.0570	0.0558
Ce, La, Di oxides.....	0.8300

The recovery of the thorium is in all cases fairly exact and the variation in the relative amounts of thorium and the other earths does not influence the sharpness of the separation. That thorium alone is precipitated by potassium trinitride is to be explained by its weak basicity. It is the weakest base in the whole group of the rare earths with the possible exception of cerium in the ceric condition, and this higher form of cerium is probably incapable of existence in the presence of hydronitric acid.

We have, then, in potassium trinitride a reagent which can be used both for the qualitative detection of thorium and for its quantitative determination either alone or in the presence of other rare earths. So far as the author is aware, this is the only method as yet devised by which one of these earths can be quickly and accurately separated from the others, and that in a single simple operation.