which the time of flow of any given liquid may be varied by varying the pressure has again been demonstrated by the discovery of the errors discussed.

WASHINGTON, D. C., AND CHICAGO, ILL.

THE SEPARATION OF THE RARE EARTHS GIVING THE MORE SOLUBLE DOUBLE SULFATES FROM BRAZILIAN MONAZITE SAND.

BY C. JAMES AND A. J. GRANT.

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The raw material for this work was supplied by the Welsbach Light Co. of Gloucester City, N. J., through the kindness of Dr. H. S. Miner, to whom the authors offer their most sincere thanks. It was prepared by treating the rare earth sulfates with potassium sulfate in a smaller quantity than that required for complete precipitation of the cerium metals. Under these conditions the greater part of the samarium and gadolinium, present, should remain in solution. The solution was then precipitated by oxalic acid.

The oxalates were converted into oxides by ignition. The conversion of oxalates to oxides is very troublesome when working on the large scale. The furnace used for this purpose was made by supporting a large $^3/_4$ inch steel plate in fire-brick. Coke was used as a source of heat.

The oxides were found to contain considerable quantities of lanthanum, cerium, praseodymium and neodymium in addition to samarium, gadolinium and the yttrium earths. Since the oxides dissolved in nitric acid with violence, the cerium content could not be very large.

The fractionation of the double magnesium nitrates is the best method for roughly splitting up such a mixture. The oxides were therefore dissolved in concentrated nitric acid, any ceric nitrate being reduced to the cerous condition by the addition of some of the original oxalates. The warm and somewhat diluted liquid was then filtered through large cloth filters, supported in such a way as to allow the liquid to run into a long trough which drained into a large earthenware receiver. Owing to the presence of so much of the yttrium earths, a quantity rather less than the theoretical amount of nitric acid was neutralized by powdered ignited magnesite. The solution of magnesium nitrate was diluted, and filtered in a similar manner to the rare earth nitrates. The solutions were mixed and evaporated until about half the solid crystallized out on cooling. The crystals were twice recrystallized and then placed aside, while the mother liquor was fractionated until the spectrum of samarium or erbium became intense. When the above condition had been reached the mother liquor was largely diluted and precipitated by means of oxalic acid. The oxalates were filtered off, dried and ignited to oxides. These last operations removed the large amounts of impurities, such as iron and aluminium, etc., which had accumulated in the most soluble end.

It was found advisable to arrange the double nitrates, which separated out at a period later than those first mentioned, according to the intensity of the neodymium color. The more soluble crystals were deeper colored and richer in neodymium.

After all the yttrium earths and practically the whole of the samarium had been removed, the double nitrates were again taken up and submitted to a further fractionation. As soon as the least soluble crystals became colorless or greenish they were removed from the series, while the crude neodymium magnesium nitrate was removed from the most soluble end.

The original material had, by this time, been roughly divided into three portions, as follows:

(*a*) Least soluble portion, forming white or greenish crystals consisting of lanthanum, cerium and praseodymium magnesium nitrates together with traces of the neodymium compound.

(*b*) More soluble crystals, colored deep amethyst, being largely composed of neodymium magnesium nitrate with traces of the double nitrates of magnesium with samarium, praseodymium, cerium and lanthanum.

(*c*) Oxides from the mother liquors containing neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium and lutecium.

The various steps can be followed by the diagram given on p. 43.

Cerium.—This element was removed from the least soluble double nitrates by dissolving them in water, and boiling the solution with potassium bromate and powdered marble. This method has been described by James and Pratt.[1] However, there are a few conditions that must receive careful attention. The solution must not be too concentrated. It should contain about 20% of the nitrates; also the volume should be kept constant. If the liquid is allowed to evaporate too much, the increased concentration gives a cerium precipitate having colloidal tendencies. A precipitate of this kind remains suspended for a long time, and it is almost impossible to decant the supernatant liquid.

The potassium bromate was added to the boiling liquid first, and as soon as bromine vapors came off, it was gradually treated with powdered marble. When the solution of the double nitrates was inclined to be basic, it was observed that the bromate did not react for some time. At times the reaction became violent, and the liquid would froth and boil over. The addition of the marble, before the first evolution of bromine, tended to keep the solution basic. Therefore, when the boiling solution did not evolve bromine after the addition of bromate, the reaction was

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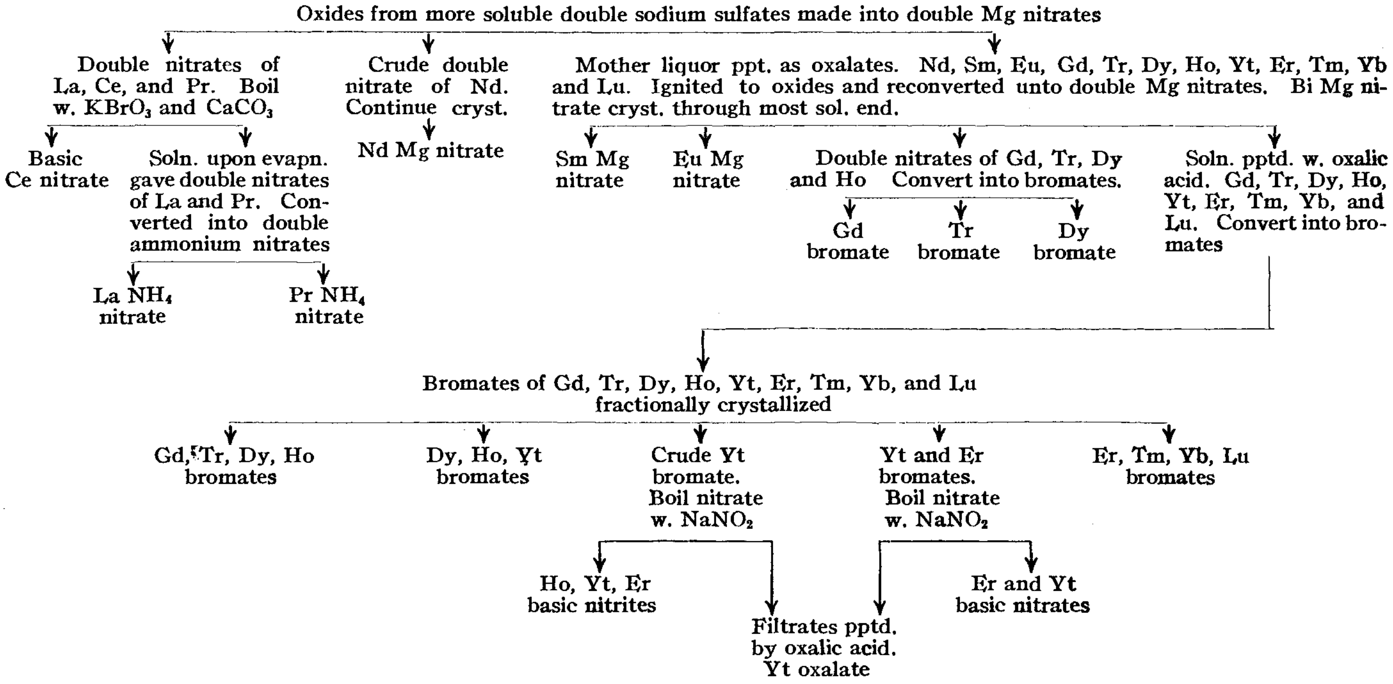
[1] This Journal, 33, 1326.


Oxides from more soluble double sodium sulfates made into double Mg nitrates
Double nitrates of La, Ce, and Pr. Boil w. $KBrO_3$ and $CaCO_3$
Crude double nitrate of Nd. Continue cryst.
Mother liquor ppt. as oxalates. Nd, Sm, Eu, Gd, Tr, Dy, Ho, Yt, Er, Tm, Yb and Lu. Ignited to oxides and reconverted unto double Mg nitrates. Bi Mg nitrate cryst. through most sol. end.
Basic Ce nitrate
Soln. upon evapn. gave double nitrates of La and Pr. Converted into double ammonium nitrates
Nd Mg nitrate
Sm Mg nitrate
Eu Mg nitrate
Double nitrates of Gd, Tr, Dy and Ho Convert into bromates.
Soln. pptd. w. oxalic acid. Gd, Tr, Dy, Ho, Yt, Er, Tm, Yb, and Lu. Convert into bromates
Gd bromate
Tr bromate
Dy bromate
La NH_4 nitrate
Pr NH_4 nitrate
Bromates of Gd, Tr, Dy, Ho, Yt, Er, Tm, Yb, and Lu fractionally crystallized
Gd, Tr, Dy, Ho bromates
Dy, Ho, Yt bromates
Crude Yt bromate. Boil nitrate w. $NaNO_2$
Yt and Er bromates. Boil nitrate w. $NaNO_2$
Er, Tm, Yb, Lu bromates
Ho, Yt, Er basic nitrites
Filtrates pptd. by oxalic acid. Yt oxalate
Er and Yt basic nitrates

started by adding a few drops of nitric acid. This procedure never failed. When the above points were followed, the cerium was rapidly thrown down in the form of a basic ceric nitrate. This precipitate settled with extreme ease and was so dense that the supernatant liquid could be entirely poured off without stirring up the deposit. When the operation had been carefully carried out, the precipitate was of a canary yellow color. Darker colored precipitates settled much more slowly. Two operations were employed for the removal of the cerium, since the last traces usually carried down some of the other earths. The first operation was continued until no action was noticed upon adding marble. The separation of the cerium was carried out in an enamelled pail, and several of these were kept going as they required very little attention when once started. Usually, the first precipitate formed about nine-tenths of the total cerium present. After the basic ceric salt had settled, the clear supernatant liquid was poured off into a pail and a rough estimate made of the cerium remaining. If only very small quantities were present, the liquid was heated to boiling and treated with a solution of sodium peroxide. When several per cent. remained the liquid was thoroughly boiled with more powdered marble. It is not advisable to add the second precipitate to a new lot of double nitrates, since it often causes the next precipitate to form badly and to be darker colored. The basic ceric nitrate was placed in large porcelain dishes and washed by decantation with boiling water containing some nitric acid. The precipitate was finally washed upon a large Büchner funnel. It was then dissolved in hydrochloric acid, reduced by alcohol and then precipitated as the sulfate or oxalate.

The cerium free liquid, from the second basic nitrate precipitate, was evaporated until about two-thirds crystallized upon cooling. The mother liquor was found to contain practically the whole of the calcium nitrate and the excess of magnesium nitrate. Only traces of the rare earths were present. The crystals were drained and placed aside for the extraction of lanthanum and praseodymium.

The cerium forming the second precipitate may be purified by repeating the process or by employing one of many other methods that have been described by vaious workers.

Lanthanum.—The double magnesium nitrates, consisting mainly of the lanthanum salt, together with small amounts of praseodymium magnesium nitrate, were dissolved in water and precipitated by means of oxalic acid. The oxalates were ignited and converted into the double ammonium nitrates. These were then recrystallized many times from water containing nitric acid. The lanthanum separated in the least soluble crystals, which were obtained quite colorless.

Praseodymium was obtained from the more soluble portions obtained during the purification of the lanthanum and from the intermediate fractions between the crude lanthanum and crude neodymium described above. Praseodymium was separated from the lanthanum by means of the double ammonium nitrates, and from neodymium by using the double magnanese nitrates. These methods have been described many times. The first having been used by Auer von Welsbach and the second by Urbain.

Neodymium.—This element was purified by the crystallization of the double magnesium nitrate.

Samarium and Europium.—The oxalates obtained from the original mother liquors were ignited to oxides. These oxides contained neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium and lutecium. The amount of celtium would be so small that it was not looked for. The scandium, if present, was probably lost during the precipitation as oxalates.

The oxides were converted back into double magnesium nitrates and fractionally crystallized from (1 to 1) nitric acid. Whenever the mother liquor failed to crystallize properly a considerable quantity of the double nitrate of bismuth and magnesium was added. This procedure rapidly removed the remaining europium and gadolinium. Whenever the mother liquor was considered free from the latter element it was removed and precipitated with oxalic acid. After continuing the fractionation for some time, the following main fractions were obtained: Crude neodymium magnesium nitrate; samarium magnesium nitrate; bismuth magnesium nitrate containing europium magnesium nitrate; gadolinium magnesium nitrate containing terbium, dysprosium, holmium and small amounts of yttrium; oxalates mainly yttrium but containing dysprosium, holmium, erbium, thulium, ytterbium, lutecium and traces of terbium.

Gadolinium and Terbium.—Gadolinium magnesium nitrate, containing terbium, dysprosium, holmium and small amounts of yttrium was dissolved in water and precipitated as the oxalate. The oxides obtained from the latter were dissolved in bromic acid, and the bromates, resulting, submitted to a long series of fractionation. Gadolinium appeared at the least soluble end in a very pure form. The fractions between gadolinium and dysprosium contained terbium. The solutions showed an absorption band in the blue, while the oxide was almost of a black color.

Dysprosium and Holmium.—There were two sources for these elements, the fractions of bromates more soluble than terbium, and the yttrium earth oxides obtained earlier. The oxides were converted into bromates by dissolving in bromic acid. The solution was evaporated and the crystals recrystallized fractionally from water. This gave:

(*a*) Least soluble-dysprosium, holmium and yttrium bromates containing traces of terbium.

(*b*) Bromate of yttrium containing some dysprosium and holmium.

(*c*) Bromate of yttrium containing very small amounts of dysprosium, holmium and erbium.

(*d*) Bromate of yttrium containing very small amounts of erbium.

(*e*) Bromates of yttrium and erbium.

(*f*) Bromates of erbium, thulium, ytterbium, lutecium and (celtium).

The least soluble portions of the bromates were mixed, according to their compositions, with the corresponding fractions forming the more soluble end from the terbium gadolinium series. After the fractionation had been continued again for a very long time, the terbium collected in the least soluble portion.

Dysprosium slowly separated from holmium.

The separation of dysprosium from terbium by the bromate method leaves much to be desired.

The preparation of holmium was not attempted. The separation of this element is one of the most difficult problems in inorganic chemistry.

Yttrium.—The raw material for the yttrium comprised fractions (*c*) and (*d*) of the bromates. Since these fractions were quite free from terbium, the best processes for the purification consist of the basic nitrate, the nitrite, the chromate and the cobalticyanide methods. The basic nitrate and the nitrite are the best for large amounts of material.

The basic nitrate method may be carried out several different ways. The nitrates may be fused and partially decomposed by heat. The fused mass is then carefully poured into cold water, and the whole well boiled. If the operation has been successful the entire mass goes into solution, and the basic nitrate separates upon cooling. Should the decomposition be pushed too far a residue will remain.

Many methods have been published which are based upon the basic nitrate principle, such as boiling the oxides with the nitrate solution, boiling the nitrate solution with magnesium oxide, boiling the nitrate solution with sodium hydroxide. However, it should be remembered that the best results are obtained when the basic nitrate separates from solution upon cooling.

The writers boiled a concentrated solution of the nitrates of yttrium and erbium, and added sodium hydroxide solution until crystals of the basic nitrate began to make their appearance. The liquid was then allowed to cool, and the rose colored crystals rich in erbium removed by filtration. The process was then repeated upon the filtrate, etc. The basic precipitates began to get paler as the yttrium concentrated. When the amount of erbium present was very small, the liquid did not readily clear up after the addition of the sodium hydroxide, but showed a tendency to become colloidal. This prevented rapid filtration from the basic nitrate, and in order to avoid this, sodium nitrite was employed to render the liquid basic. Any precipitate which formed during this operation filtered easily.

When a concentrated solution of the nitrates is boiled with sodium nitrite, a basic nitrate results. In the case of a dilute solution, a basic nitrite separates as a granular precipitate during the boiling.

The yttrium was further purified by boiling the diluted nitrate solution with sodium nitrite. This gave a very pure product, which in solution showed no absorption of erbium.

The separation of erbium, lutecium, ytterbium, thulium and celtium was not attempted with this material.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

OXIDATION AND REDUCTION WITHOUT THE ADDITION OF ACID.

II. THE REACTION BETWEEN STANNOUS CHLORIDE AND POTASSIUM DICHROMATE. A CONTRIBUTION TO COLLOID-CHEMISTRY.

BY MARKS NEIDLE AND JOSHUA C. WITT.

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It may be stated from the results of the first paper of this series that colloidal hydrous oxides or hydroxides are obtained in an oxidation-reduction reaction, in which acid must be added for the formation of normal salts, if the stoichiometric relation is the same without acid as with acid. If the reaction involves ions which are good precipitants of the colloids formed, precipitation takes place; otherwise, hydrosols are obtained.

The equation for the reaction between stannous chloride and potassium dichromate, with acid, is

$$3SnCl_2 + K_2Cr_2O_7 + 14HCl = 3SnCl_4 + 2CrCl_3 + 7H_2O + 2KCl,$$

where, it is seen, fourteen mols of hydrochloric acid per mol of dichromate are necessary to form the normal salts of tetravalent tin, trivalent chromium, and of potassium. The object of this investigation was to determine whether the stoichiometric relation between dichromate and stannous chloride is the same, *i. e.*, one mol of the former oxidizing three mols of the latter, and what substances are formed when no acid is added.

The Stoichiometric Relation.

Samples of commercial C. P. stannous chloride of about 0.4 g. each were rapidly transferred to beakers from a weighing bottle, dissolved in 50 cc. of water, and the solutions titrated with standard dichromate, some after adding 10 cc. of concentrated hydrochloric acid and others without the