The Mechanism of a Chromate Process for the Separation of the Lanthanons and Yttrium.

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Lanthanon separations have been divided into two classes: those based on differences in solubility of salts, in which yttrium is interpolated in the heavy lanthanons between holmium and erbium, and those based on differences in basicity, in which it is interpolated in the middle lanthanons between gadolinium and terbium. From a mixture containing both middle and heavy lanthanons yttrium can be rapidly concentrated by a chromate process which combines both solubility and basicity separations in one operation; by the addition of a base to a lanthanon dichromate solution, the strongly basic lighter lanthanons are precipitated as double or normal chromates, while the weakly basic heavier lanthanons are removed by hydrolysis as basic salts.

Many procedures for the separation of the lanthanons and yttrium have been recommended, but the results could not be critically compared owing to the absence of reliable analyses. With the advent of spectrophotometry it is now possible to compare the various methods and to understand more fully the mechanisms involved. The aim of this investigation was to define a method for producing a fairly pure yttria from a material containing middle and heavy lanthanons. A number of procedures were compared involving fractional crystallization, precipitation, and decomposition, and it was found that the results could be grouped into three classes according to the mechanism involved, *i.e.*, separations achieved by differences in solubility of salts, by differences in basicity, and by the chromate procedure described below, the mechanism of which this paper is intended to clarify.

It is generally agreed that in separations based on differences in solubility of normal salts, whether by fractional crystallization of soluble salts, *e.g.*, bromates, or by fractional precipitation of sparingly soluble compounds, *e.g.*, double alkali sulphates, yttrium is interposed in the lanthanon sequence between holmium and erbium. The position of yttrium in a basicity separation is not satisfactorily established, however, the situation being undoubtedly complicated by the loose interpretation of the term basicity and the phenomena attributable to it. The situation has been reviewed by Moeller and Kremers (*Chem. Rev.*, **1945**, **37**, 97), who quote a number of different " orders of decreasing basicities " arrived at experimentally by various authors. The position of yttrium in the lanthanon sequence is reported as varying from between neodymium and samarium to between holmium and erbium, but in general is reported earlier in the sequence than for solubility separations.

Although chromate precipitation of the lanthanons has been much used for separating yttrium, no clear exposition of the mechanism has been given. Krüss and Loose (*Z. anorg. Chem.*, **1893**, **3**, 92) observed that didymium chromate could be precipitated by potassium chromate from a cold neutral nitrate solution of gadolinite earths, but a precipitate high in erbium was obtained on heating, and dichromate formation in the reaction liquor occurred. Britton (*J.*, **1924**, **125**, 1875) found that from 0·13M-solution only normal lanthanum and cerium chromates were precipitated, other lanthanon chromates being too soluble at pH values below the hydroxide precipitation figure to allow of solid normal chromate formation. However, by working with stronger solutions they appear to be obtainable. It is, moreover, evidently possible in the one reaction to obtain normal chromates of the strong bases and basic chromates of the weak bases. The majority of workers using the chromate process for separations adopted Muthmann and Böhm's technique (*Ber.*, **1900**, **33**, 42; *Z. angew. Chem.*, **1902**, **15**, 1282), that of slowly adding potassium chromate solution to a hot stirred dichromate solution of the lanthanons; a variant adopted for the present study was to cause precipitation by the addition of alkali instead of potassium chromate.

EXPERIMENTAL

Analysis.—All fractions were analyzed spectrophotometrically for certain lanthanons in neutral chloride solutions. Beer's law was found to hold adequately for dysprosium, holmium, erbium, thulium, and ytterbium, but not for gadolinium owing to incomplete resolution of its very sharp absorption bands, and a calibration curve was constructed from a pure gadolinium standard.

Starting Material.—Comparative runs were carried out on a crude yttrium oxide containing a high percentage of middle lanthanons, an analysis of which showed: Nd_2O_3, 0·1; Gd_2O_3, 19·7; Dy_2O_3, 16·0; Ho_2O_3, 2·2; Er_2O_3, 3·4; Y_2O_3, 58·6%. Light lanthanons, as shown by neodymium, were negligible, having been previously removed by double alkali sulphate precipitation; thulium and ytterbium were sought spectrophotometrically but not positively identified and were therefore of low order, and a small amount of terbium was indicated by the colour of the oxide; after analysis for gadolinium, dysprosium, holmium, and erbium, the rest was almost entirely yttrium which was estimated by difference, checked by occasional atomic-weight determinations.

Solubility Separations.—As an example of solubility separation, the fractional precipitation of the double alkali sulphates has been chosen for direct comparison with the chromate procedure. About 100 g. of oxide were converted into 1 l. of chloride solution and fractionally precipitated by slow addition of finely powdered anhydrous sodium sulphate to the cold stirred solution. Analyses of the oxides from the fractions obtained are shown in Table 1; the order of precipitation is clearly Nd, Gd, (Tb), Dy, Ho, Y, and Er, the last two apparently coming out at about the same rate, although this point cannot be definitely established owing to the difficulty of accurate determination of the small percentage of erbium present and the inclusion of small amounts of other lanthanons in the yttrium figure. A good removal of middle lanthanons has been obtained, but erbium is concentrated with yttrium. The same order was shown by fractional crystallization of soluble salts, *e.g.*, nitrates.

TABLE 1. *Composition (%) of oxides obtained from fractional precipitation of lanthanons with sodium sulphate.*

Fraction	% of Total Ln_2O_3 * removed	Composition (%)					
		Nd_2O_3	Gd_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Y_2O_3
1	13	1·2	56·2	15·2	1·1	1·9	24·4
2	23	0·2	38·0	20·4	1·8	2·2	37·4
3	13	—	19·5	24·3	2·5	3·0	50·7
4	15	—	6·9	21·0	3·0	3·9	65·2
5	8	—	1·0	17·7	3·1	4·5	73·7
Final liquor	28	—	—	6·0	2·1	4·9	87·0

* Including yttrium.

Basicity Separations.—A number of these were examined, involving fractional precipitation by magnesia or ammonia at different concentrations, and fractional decomposition of the nitrates. The last is described here as an example of the type of results obtained. About 100 g. of oxide were converted into nitrate and fused until decomposition of the nitrate began; the melt was then held at 310° for 10 min., then poured rapidly into 700 ml. of cold water. Almost all the melt could be added before precipitation of the basic nitrate commenced; this was complete on storage overnight. The precipitate was filtered off (fraction A), the solution boiled down, and the fusion repeated at 10° intervals to yield further fractions. Analyses of the oxides from the fractions obtained are shown in Table 2. The order of precipitation is clearly

TABLE 2. *Composition (%) of oxides obtained from fractional decomposition of lanthanon nitrates.*

Fraction	% of total Ln_2O_3 * removed	Composition (%)					
		Nd_2O_3	Gd_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Y_2O_3
1	11	—	9·8	25·2	3·8	7·4	53·8
2	11	—	13·2	23·7	3·4	6·1	53·6
3	11	—	15·2	22·9	3·2	5·3	53·4
4	13	—	18·0	20·2	2·7	4·1	55·0
5	11	—	18·9	18·2	2·3	3·3	57·3
6	11	0·1	22·1	15·0	1·9	2·4	58·5
7	8	0·2	26·0	12·3	1·5	1·9	58·1
Final liquor	24	0·6	31·9	5·4	0·7	1·0	60·4

Er, Ho, Dy, Tb, Y, Gd, Nd (the position of terbium was shown by the colours of the oxides, which became progressively lighter). The identical order and a very similar degree of separation was shown by fractional precipitation by magnesia or ammonia.

Chromate Separations.—Earlier work in these laboratories on the use of the chromate procedure described below for the separation of the light lanthanons had already confirmed the formation of an insoluble double alkali chromate according to the equation

$$2Ln(NO_3)_3 + 2K_2Cr_2O_7 + 4KOH = K_2CrO_4,Ln_2(CrO_4)_3 + 6KNO_3 + 2H_2O$$

To 100 g. of oxide as nitrate solution were added 216 g. of potassium dichromate (the theoretical requirement of the above equation), and the mixture was made up to 1 l. The resulting solution was kept near the b. p. with continuous stirring while the material was precipitated fractionally by dropwise addition (1 hr.) of 125-ml. portions of 10% sodium hydroxide solution, followed by a further hour's digestion. The precipitates were filtered off, and converted into oxides *via* two oxalations. Analyses of the oxides from the fractions obtained are shown in Table 3. The order of precipitation is now Nd, Gd, (Tb), Dy, Ho, Er, Y, with erbium concentrating slightly initially, but being rapidly removed towards the end.

TABLE 3. *Composition (%) of oxides obtained from fractional precipitation of lanthanon chromates with sodium hydroxide.*

Fraction	% of total Ln_2O_3 * removed	Composition (%)					
		Nd_2O_3	Gd_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Y_2O_3
1	20	0·9	39·9	27·0	2·6	3·6	26·0
2	24	0·2	29·4	24·0	2·9	4·2	39·3
3	21	—	21·2	16·3	2·8	4·5	55·2
4	19	—	9·1	6·5	1·8	3·2	79·4
5	14	—	—	1·3	0·5	1·3	96·9
Final liquor	2	—	—	0·4	0·2	0·4	99·0

DISCUSSION

Although the results for solubility separations need little comment, confirming what has been reported previously, those for basicity separations warrant further investigation. The basicity procedures investigated, *viz.*, nitrate decomposition, and magnesia or ammonia precipitation at different concentrations, all agreed on the order of basicity as Nd, Gd, Y, Tb, Dy, Ho, Er; further, the degree of separation was similar for all, strongly suggesting that equilibria were approached between the lanthanons themselves irrespective of the means of precipitation. The results disagree with the majority of earlier reports on these techniques, which regard the basicity of yttrium as comparable with that of the light lanthanons, placing it between neodymium and samarium. They are, however, in agreement with the data on physicochemical investigations of equilibria between hydroxyl and lanthanon ions collected by Moeller and Kremers (*loc. cit.*) which place yttrium between gadolinium and erbium, lack of data excluding a more precise placing. These authors regard this as evidence in favour of their theoretically deduced basicity of yttrium between dysprosium and holmium, whereas the results above agree with Endres (quoted by Moeller and Kremers, *loc. cit.*) in placing it between gadolinium and dysprosium.

TABLE 4. *Composition (%) of oxides obtained by J. K. Marsh from fractional precipitation of weakly basic lanthanon chromates with sodium hydroxide.*

Fraction	% of total Ln_2O_3 * removed	Composition (%)			Fraction	% of total Ln_2O_3 * removed	Composition (%)		
		Er_2O_3	Tm_2O_3	Yb_2O_3			Er_2O_3	Tm_2O_3	Yb_2O_3
1	12	12	4·0	33	4	15	3·2	0·7	2·8
2	48	11	2·4	21	Final liquor	6	0·8	—	—
3	19	6·1	1·4	7·3					

* Including Y_2O_3.

It is now obvious that the most convenient procedure for obtaining yttrium from a concentrate containing middle and heavy lanthanons requires two stages: a solubility separation to remove the middle lanthanons and concentrate yttrium with the heavy lanthanons, followed by a basicity separation to remove the heavy lanthanons. The success of the chromate method is readily explained by assuming that these two requirements are met in one operation. In the presence of a high concentration of dichromate, initial addition of sodium hydroxide causes precipitation of the strong bases as double or normal chromates; as with the sodium sulphate precipitation, light lanthanons, gadolinium, terbium, and some dysprosium are removed, leaving yttrium and erbium in the liquor. As the pH and the dilution of the solution increase on further addition of sodium hydroxide, hydrolysis becomes increasingly effective and basic chromates of the weak bases are precipitated; the heavy lanthanons are removed, leaving yttrium in solution.

Support for this mechanism is given in a personal communication from J. K. Marsh, who found that application of a similar chromate procedure to a nitrate solution of weakly basic lanthanons, using sodium dichromate and sodium hydroxide, resulted in their precipitation in reverse order of basicity, *i.e.*, ytterbium, thulium, erbium; his results are given in Table 4. Further support is given by the nature of the precipitate, which, during the run shown in Table 3, changed from bright orange, dense, readily filterable crystals in the early fractions to a pale yellow flocculent hydrate-type material at the end. Moreover, although the equation given above obviously does not hold throughout the fractionation, when the potassium dichromate initially present was decreased to 75% of its requirement, or if the initial oxide concentration was reduced to 30 g./l., a considerably poorer separation of gadolinium and terbium resulted. Both alterations favour the basicity separation, and unless these two elements are removed during the initial solubility separation stage, they persist in the last fractions by reason of their comparatively high basicity.

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